1975

Some Effects of Decomposing Plant Residues and Soil Moisture on the Extractable Manganese Content of Four Soil Types.

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SOME EFFECTS OF DECOMPOSING PLANT RESIDUES AND SOIL MOISTURE ON THE EXTRACTABLE MANGANESE CONTENT OF FOUR SOIL TYPES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Horticulture

by
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December, 1975

ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. Leon Standifer for his assistance and guidance during the course of this investigation.

Appreciation is also expressed to the staff members of the soil testing laboratory of Louisiana State University for their kind assistance with the chemical analyses, and to Mr. R. D. Delaune of the Agronomy Department, L.S.U., for his willing assistance and suggestions, and to Dr. L. G. Jones for facilitating his laboratory and for reviewing the manuscript.

He is also thankful to Mr. Salvador Alemany, Dean of the College of Agricultural Science, U.P.R.; Mr. F. Sanchez-Nieva, Director of the Agricultural Experiment Station, U.P.R., and Dr. E. Hernandez, Head of the Department of Agronomy, Agricultural Experiment Station, U.P.R., for arranging financial assistance.

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ABSTRACT

A series of growth chamber, greenhouse and field experiments was conducted during the period 1973-75 directed toward finding whether decaying vegetative matter could cause an increase in soil extractable Mn and thus be a contributing factor in the development of Mn toxicity, especially in wet soil conditions.

The incubation technique was used in the growth chamber and greenhouse experiments to determine the influence of applied plant residues and moisture level on the extractable Mn status, pH and redox potentials of four soil types and also their effects on the germination, vegetative yield and Mn concentration of soybean seedlings.

Flooding the soil resulted in striking increases in extractable Mn, especially in Olivier silt loam soil. Additions of Alfalfa meal to flooded soils caused further increases in the extractable Mn contents of Olivier silt loam, Sharkey clay, and Commerce silt loam soils, but had no effect in Convent sandy loam soil. Increasing the soil moisture to 60 percent resulted in redox potential values characteristic of reduced soils. The drop in redox potentials from flooding was more pronounced generally in soil containing increasing amounts of applied Alfalfa meal. There was a strong tendency for soils of low pH to decrease in acidity and for soils of high pH to increase in acidity upon flooding. Applied Alfalfa meal favored the development of higher pH values in acid soils.

Applications of Alfalfa meal at 2 and 4 percent markedly reduced the germination of soybean seedlings and consequently the vegetative yields. The Mn concentration in the soybean seedlings was markedly increased by flooding, while applied Alfalfa meal showed variable effects and no clear-cut trend was evidenced. The extractable Mn content was highest for Olivier, intermediate for Sharkey and Commerce, and lowest for Convent soil. A similar trend was observed with the uptake of Mn by soybean seedlings.

A special technique was used in the field experiment which allowed the study of several soil types together in a small replicated field experiment. This factorial experiment consisted of three cover crop species arranged in the main plots and three soil types constituting the sub-plots.

Soils in plots under cover crops contained a lower amount of extractable Mn than that in the control plots, and also showed lower pH values. Wetting the soil for a period of 5 days resulted in a marked drop of the redox potential values. The redox potential values, however, were not significantly affected by cover crop species or soil type.

Soybean seedlings grown in plots containing decomposing roots of cover crops showed lower Mn concentration than those grown in the control plots. There was a significant positive relationship between Mn concentration in seedlings and soil extractable Mn.

INTRODUCTION

For several years the Horticulture Department of Louisiana State University has been studying a system of multiple cropping under conditions where wet soil may cause substantial delays in seedbed preparation. This system employs the concept of minimum tillage in which all weeds are controlled with herbicides and raised seedbeds are utilized to provide drainage. After harvest, the old crop plant residues are cut to ground level and the next crop is immediately planted through the stubble. Mechanical planting without any appreciable delay due to wet soil is possible because water furrows are kept firm and have a slight slope (0.5%).

If this system can be commercially implemented, it would allow much more efficient utilization of productive land in tropical and subtropical areas.

Although the program has been generally successful, a problem of crop toxicity sometimes occurs when southern peas (*Vigna sinensis* L.) are planted in the decaying stubble of sweet corn (*Zea mays* L.). In 1972, developing pea seedlings showed symptoms of severe manganese toxicity. Chemical analysis of leaves from affected plants indicated manganese levels of 5,000 to 7,000 ppm. Despite this severe toxicity most of the plants recovered within a few weeks and produced a normal but delayed yield.

This test was conducted on Olivier silt loam, a typical Mississippi Terrace soil with normally high levels of oxidized manganese. Cotton and soybeans grown on this soil frequently develop Mn toxicity during wet periods if the pH is below 5.5. However, soil samples taken from this test two months later showed the pH to be in the range of 6.0 to 7.0.

Because the field had been subjected to almost daily rains during the week that the pea seedlings were emerging from the soil, it was postulated that the problem involved temporary reduction of Mn related to rapid decomposition of corn roots in wet soil.

A survey of pertinent literature showed that most studies of Mn toxicity in wet soils concerned rice culture and did not directly relate to this study. It was also evident that the problem could involve several variables which would be difficult to control.

The present investigation was initiated to develop techniques for evaluating several factors which might be involved in the apparent Mn toxicity of pea seedlings in the field test of multiple cropping.

LITERATURE REVIEW

Chemistry of Manganese in Soil

Manganese is extremely complex in its chemical behavior. Only divalent Mn is adsorbed and accumulated in plants. Manganese in soil can be divided into water-soluble form, exchangeable available, and relatively insoluble higher oxides of Mn, all of which are in equilibrium. The highly insoluble oxidized forms of soil Mn exist primarily as oxides at various degrees of reactivity, while the more soluble divalent ion occurs in the soil solution or on the exchange complex in the soil. The form of Mn which predominates at any one time is dependent on the soil pH, moisture tension, oxidation-reduction status, organic matter content and microbial activity of the soil.

Soil reaction has a pronounced effect on the transformation of Mn. According to Leeper (1947), soils with a pH below 5.5 may contain most of their Mn in the water-soluble and/or exchangeable form. Neutral and alkaline conditions favor the formation of highly insoluble higher Mn oxides (Sherman and Harmer, 1942). At all pH values above 5.5, soil organisms can oxidize the divalent form (Leeper and Swaby, 1940); this oxidation is rapid in well-aerated soils, especially in the pH range of 6.0 to 7.5. The reverse reaction also occurs. The higher oxides are reduced, whether by direct reaction with organic matter or by biological processes. Reduction by organic matter is more likely at low pH values, since the oxidizing power of the higher oxides increase rapidly with acidity (Leeper, 1947). Biological reduction can take place at any pH value if the oxygen tension is low, when the anaerobic bacteria use the higher oxides as a source of oxygen.

Rivenbark (1961) concluded from his review of literature that soil Mn is oxidized by both chemical and biological means. Contrary to this, Heintze and Mann (1949), Heintze (1957), and Page (1962) suggested that the disappearance of divalent Mn above pH$_7^{\prime}$ may be the result of the formation of Mn-organic matter complexes especially in organic soils.

Hammes and Berger (1960) measured the release (accumulation of divalent Mn ions) of manganese on drying of a soil and reported that the release was not a simple dehydration phenomenon. The release of Mn on heating of a soil has been observed by Fujimoto and Sherman (1948).

Sherman et al. (1942) were among the first to indicate that a dynamic equilibirum between divalent Mn and the insoluble higher oxides was apparent in the soil. Mann and Quastel (1946), and Dion and Mann (1946) have proposed Mn cycles in soils. Using isotropic techniques and a successive extraction scheme based on the solubility characteristics of the various Mn forms, Rivenbark (1961) suggested the following equilibrium cycle:

$$
\begin{array}{ccccc}
\text{Exchangeable Mn} & & \xrightarrow{\text{Biological oxidation}} & & \text{Trivalent oxides} \\
\downarrow\uparrow & \searrow\nwarrow & & \nearrow\swarrow & \downarrow\uparrow \\
\text{Water-soluble Mn} & & \text{Divalent oxides} & & \text{Trivalent oxides}
\end{array}
$$

There is, however, no general agreement on the components of the equilibrium cycle.

Seasonal Variations of Manganese

The availability of many elements in soils varies considerably from one part of the year to another. Manganese exhibits the most pronounced seasonal variation in availability (Hodgson, 1963), probably due to the microbially induced reduction and oxidation. McCool (1934) first noted that water-soluble Mn was high during the summer months. Dorph-Petersen (1950) found 5 to 10 times as much exchangeable Mn in summer as compared to winter. Sherman and Harmer (1942), on the other hand, claim that winter favors manganous and summer favors manganic forms of the element. This conclusion was based on work with more alkaline soils than the earlier reports.

Some authors emphasize short-term fluctuations in availability over seasonal ones. De Long et al. (1940) could find no seasonal trends, but they noted that the Mn extracted with 0.2 N acetic acid increased following each rainfall. Kosegarten (1956) observed that exchangeable Mn increased following rainy periods and easily reducible Mn underwent a corresponding decrease.

Manganese Uptake by Plants

The total content of Mn in soils does not reflect the ability of the soil to supply Mn to plants, if that ability is measured in terms of the actual uptake by the plant. Leeper (1947) dismissed total Mn in soil as irrelevant to the problem of the deficiency disease "grey speck" of oats and "marsh spot" of peas. Adams and Wear (1957) showed that the development of "crinkle leaf" (Mn toxicity) in cotton was related to the level of water-soluble Mn in soil. Forsee (1954) working with organic soils in Florida, found water-soluble Mn less reliable than exchangeable Mn in determining the amount of Mn taken up by the plant. Stenuit et al. (1956) could find no relationship between water-soluble Mn of various soils and the occurrence of "grey speck" of oats. A highly significant correlation between exchangeable soil Mn and the Mn content in the upper leaves of peanut was obtained by Rich (1956).

Some neutral salts, KCl, NaCl (York et al., 1954) and $CaCl_2$ (Foy, 1964), have increased the manganese content of plants and the exchangeable Mn level in acidic soils. Hamilton (1966) found a positive correlation between Cl^- concentration and Mn uptake by oats. The Cl salts also increased the Mn content of bush beans and sweet corn more than $SO_4^=$ and $CO_3^=$ salts in acidic soil such that Mn toxicity symptoms were present in the Cl salt treatments (Jackson et al., 1966).

Manganese Extracting Solutions

Numerous soil extractions for evaluating the Mn status of soils have been proposed. In general, there are three basic methods for extracting soil Mn: one is the use of various salts at different degrees of concentration; another employs the use of acid as extractants; and the third involves the use of mild reducing agents. Several modifications have been introduced to the above-mentioned methods such as variation in extracting time, concentration of extractant, ratio of soil to extractant, and pH to which extractant is buffered.

Two commonly used extractants are water and ammonium acetate (NH_4OAc) (Adams, 1965). Sodium acetate together with ammonium acetate and other salt extractants are generally considered to remove the exchangeable Mn from the soil. Other salt solutions used to estimate the available Mn are $Mg(NO_3)_2$ and $Ca(NO_3)_2$ (Boken, 1955, 1956, 1958; Jones and Leeper, 1951; Rivenbark, 1961).

Piper (1931) found that extraction of the soil with a mild reducing agent gave better correlation with the Mn taken up by plants than did the determination of water-soluble and exchangeable Mn. He called that released by extraction with hydroquinone "easily reducible" manganese. Sherman et al. (1942) determined what they called active Mn, which was the sum of the exchangeable and water-soluble fraction plus easily reducible Mn estimated by 6-hour extraction of soil with neutral normal NH_4OAC containing 0.2% hydroquinone.

The water-extractable levels would seem appropriate for predicting toxicity since plant uptake is related to the levels of divalent Mn in either a soil solution or a nutrient solution (Berger and Gerloff, 1947 and Morris, 1948). However, because water-soluble and exchangeable Mn levels are dependent upon changes in soil pH, moisture content, and organic matter additions, as well as treatment of samples prior to analysis (Fujimoto and Sherman, 1945); Morris, 1948; and Mulder and Gerretsen, 1952), predicting toxicity situations is difficult. Morris (1948) reported that among 25 acid soils, those with a high water-extractable Mn level also had a high exchangeable Mn level, although exceptions were noted. Fergus (1953) reported a good correlation between exchangeable soil Mn and Mn uptake by beans (*Phaseoeus vulgaris* L.) on a Mn Toxic soil. A combination of NH_4OAc-extractable Mn and soil pH provided the best means for predicting Mn uptake by maize (Zea mays L.) in a study of eight soil tests by Browman et al. (1969).

Manganese Phytotoxicity

Manganese is generally considered to be one of the more important toxic metals in acid soils (Pearson and Adams, 1967). The occurrence of Mn toxicity in plants has been well established, mainly from experiments using non-soil cultures, such as in the work reported by Ovellette and Dessureaux (1958) and by Sutton and Hallsworth (1958). It is also known that Mn occurs in naturally acid soils in sufficient quantities to be toxic to some plants (Adams and Wear, 1957 and Foy, 1964).

Wallace et al. (1945), using sand culture techniques, reported that the characteristic field acidity leaf symptoms, namely, internal chlorosis and necrotic spottings of runner beans and incurled leaf margins of cauliflower were due to toxicity of Mn. Sherman and Fujimoto (1946) concluded that the "yellow leaf fringe" in lettuce was due to Mn toxicity and could be controlled by addition of lime or mulch to the soil.

Millikan (1947) described a characteristic type of leaf necrosis in flax when Mn concentration in the nutrient solution was 25 ppm or more. Identical symptoms were also produced in highly acid soils by heavy applications of manganese sulfate.

Lingle et al. (1961) reported that severe marginal and interveinal chlorosis and necrosis of the older leaves of brussel sprouts was associated with excessive Mn content of the leaves. 1000 ppm Mn in leaves showed Mn toxicity. Jacobson and Swanback (1932) reported tobacco to be susceptible to Mn toxicity which occurs in certain soils in Connecticut. The amounts found in affected plants ranged from 5,250 to 11,670 ppm.

Neal and Lovett (1938) reproduced the typical symptoms in cotton plants known as "crinkle leaf" in sand culture by the addition of manganese sulfate to the nutrient solution. They indicated that crinkle leaf of cotton is fairly common in certain Lintonia and Olivier silt loam soils in Louisiana and is generally associated with a low pH and high amounts of soluble Mn in the soil.

White (1970) studied the effect of lime upon soil and plant Mn levels in an acid soil. He reported that Mn toxicity symptoms were observed at tissue Mn levels of approximately 1000 ppm in beans (*Phaseolus vulgaris* L.), 550 ppm in peas (*Pisum satinum* L.), and 200 ppm in barley (*Hordeum vulgare* L.). He also found that water-soluble and exchangeable Mn levels in the soil were well correlated with pH and tissue Mn levels.

Gallager (1967) observed necrotic lesions on the leaflets and petioles of celery grown in a reclaimed deep acid peat soil in the Raheen series. The Mn content of the mature leaves ranged from 245 ppm in healthy plants to over 10,000 ppm in severely affected plants.

Cannon (1971) reported Mn toxicity to sweet potato plants in sulfur treated plots at concentrations ranging from 5,000 to 12,000 ppm, but no Mn toxicity symptoms were present when the Mn concentration in the leaves was 1,000 ppm.

In an experiment designed to determine the Mn requirements for soybean, Robertson et al. (1973) reported optimum yield of soybeans when the

Mn content of leaves was 72 ppm. Reduced yield was observed when soybean leaves had Mn contents of 119 ppm. They suggested that the yield reduction was possibly due to toxic amounts of Mn.

Grassmanis and Leeper (1966) indicated that apples and pears suffered from Mn toxicity when grown under irrigation on acidified soils, on waterlogged soils, or on peculiar near-neutral soils. The degree of toxicity was related to the rate at which the Mn was reduced (on dry, moist or wet soils) and the rate at which it was biologically oxidized in moist soils.

Manganese toxicity has also been reported in dwarf beans by Lohnis (1951), in Kale, Potatoes and Sugar beets by Plant (1953), and tobacco by Hiatt and Ragland (1963) who observed chlorosis and necrotic spottings on tobacco growing in solution culture when the Mn content in the tissue reached about 3,000 ppm.

Effects of Organic Matter on Manganese Transformations

Conflicting reports are available regarding the role of organic matter on the distribution, mobilization and availability of Mn in soils. Leeper and Passioura (1963) suggested that Mn is not held in a complex form with organic matter while Main and Schmidt (1935) reported that Mn may form chelate complexes with certain components of organic matter. Misra and Mishra (1969) observed that humic acid did not appreciably increase the Mn retention by soils and suggested that perhaps other fractions, such as fulvic acid might be of importance; whereas, Pavanasasivam (1973) reported that fixed Mn is significantly and positively correlated with soil humic but not with fulvic acid.

According to Hodgson (1963), the effect of organic matter on Mn transformations in soils should take at least three forms: (1) the production of complexing agents that effectively reduce the activity of the free ion in solution, (2) a decrease in the oxidation potential of the soil, either directly or indirectly through increased microbial activity, and (3) a stimulation of microbial activity that results in incorporation of Mn in biological tissue.

The formation of complexes of Mn with organic matter has been postulated by Forsee (1954), Jones and Leeper (1951), and Page et al. (1962) as an explanation for the observed decrease in Mn availability with increasing soil pH. Main and Schmidt (1935) reported that Mn may form chelate complexes with alpha hydroxy and dicarboxylic acids.

Fujimoto and Sherman (1948), Christensen et al. (1951), and Gotoh and Yamashita (1966) reported that the reduction of Mn was favored by the presence of readily decomposable organic matter. Mulder and Gerretsen (1952) indicated that at high pH values soil organic matter may reduce higher Mn oxides to Mn^{++} and that this reduction may proceed either by direct reaction with organic matter or by biological process.

Biological Transformations of Manganese

Alexander (1961) indicated that microorganisms may affect ion availability in the soil in five ways: (1) release of inorganic ions during the decomposition of organic materials, (2) immobilization of ions by incorporation into microbial tissue, (3) oxidation to a less available form, (4) reduction of an oxidized form under conditions where oxygen is limited, and (5) indirect transformations, changes in pH, or oxidation potential.

By far the most studied and probably the most important microbiological effect on the availability of micronutrient involve the oxidation and reduction of iron and manganese. There are indications that microorganisms control the oxidation state of Mn and that changes in pH and oxidation potential have their effect only through microbial activity (Hudgson, 1963). Studies reported by Timonin and Giles (1952), Martin (1953), and Forsee (1954) have shown that soil sterilization increases the availability of Mn.

Beijerinck (1913) first reported that soil organisms could oxidize Mn. He observed when soil was added to an agar medium containing $MnCO_3$, that concretions of MnO_2 were produced. Other investigators, Bromfield and Sherman (1950) later identified a member of soil bacteria and fungi that are effective in oxidizing Mn. Active organisms include strains of the bacterial genera <u>Aerobacter</u>, <u>Bacillus</u>, and <u>Pseudomonas</u> and of the fungal genera <u>Cladosporium</u> and <u>Cephalosporium</u> (Alexander, 1961).

Gerretsen (1937) developed a technique for the direct demonstration in soil of microbial manganese oxidation. In this technique the manganous ion was allowed to diffuse through a suspension of soil in agar. On incubation it was observed that rings of dark-colored microbial growth occurred and that the cells of these microorganisms contained manganic oxides. These results were confirmed by Leeper and Swaby (1940) and Maclachan (1941).

Of particular interest is the role of bacteria in gray speck disease in oats. This disease is commonly interpreted as resulting from a deficiency of Mn. Samuel and Piper (1929) showed that if oats were supplied with less than 14 ppm Mn, gray speck symptoms developed. But later Gerretsen (1935) found that if the system was sterile, the Mn level could drop to 5 ppm without Mn déficiency being observed. If the solution were inoculated with fresh soil, gray speck appeared, but if the soil was sterilized first, it did not. The general conclusion is that organisms attracted to the rhizosphere oxidized and precipitated Mn as it approached the area of the root. Timonin (1946) further showed that oat varieties particularly susceptible to gray speck had higher proportion of Mn-oxidizing bacteria in their rhizosphere than did non-susceptible varieties.

Several studies have demonstrated that microbial oxidation of Mn is a pH dependent phenomenon (Gerretsen, 1937; Leeper and Swaby, 1940; Fujimoto and Sherman, 1948; and Reid and Miller, 1963). At reactions more acid than pH 5.5, Mn is present largely as exchangeable and is chemically oxidized to manganic oxides. Below pH 8.0, there is little chemical oxidation of divalent Mn, the process of Mn^{++} autooxidation being characteristic of low hydrogen ion concentrations.

$$MnO_2 + 4H^+ + 2e^- \underset{\text{alkaline}}{\overset{\text{acid}}{\rightleftharpoons}} Mn^{++} + 2H_2O$$

In the intermediary ranges, between pH 5.5 and 8.0, the predominance of microbial phenomena becomes evident, although microbial oxidation occurs more rapidly between pH 6.0 and 7.5.

During the cyclic sequence of Mn transformations, the divalent ion may be regenerated through acid production or by microbial reduction. Leeper (1947) noted that biological reduction can occur at any pH value if the oxygen tension is low. MnO_2 is capable of functioning as an electron acceptor in anaerobic respiration (Mann and Quastel, 1946; and Ponnamperuma, 1965).

The reduction of Mn in soils is an energy-requiring process so that the importance of microbial activity can be demonstrated by the addition of easily decomposable organic matter (Rao, 1956; and Hoschster and Quastel, 1952).

The isolation and study of Mn reducing microorganisms has received very little study. Among the Mn reducing bacteria are members of the genera Bacillus, Vibrio, Clostridium, and Pseudomonas (Ehrlich, 1964; and Troshanov, 1969).

Harmful Effects of Organic Residues Decomposition

The return of plant residues to the soil has long been regarded as being of agronomic importance especially as related to tilth and maintenance of organic matter. Such practice, however, sometimes results in deleterious effects in succeeding crops. The precise mechanism of the injurious effects on plants is not clearly understood. Some investigators attribute the harmful effects of crops to the depletion of nutrients or immobilization of nitrogen by soil microorganisms during the decomposition process (Millard, 1957; and Ripley, 1941). Others have suggested that the harmful effects were mainly due to their influence on the microbiological balance with the resulting effect on the survival and virulence of many soil pathogens (Garret, 1956; Miller, 1931; and Sanford, 1946).

Several workers (McCalla and Haskins, 1964; Patrick and Koch, 1958; Shreiner and Shorey, 1909; and Patrick and Toussoun, 1965) have noted that the decomposition of plant organic matter in soil is often accompanied by formation of substances with phytotoxic properties. Patrick et al. (1963) reported that the most severe phytotoxicity occurred in fields where decomposition of plant organic matter had taken place in cold wet soil during early stages of decomposition. The same authors reported that when conditions were optimum for phytotoxic formation, type of plant material and soil type appeared to have little effect on over-all phytotoxicity. Toussoun et al. (1967) noted that the production of water-soluble phytotoxin during decomposition of barley residue in soil in the laboratory was unaffected by temperature between 16 and 24^{o}C but required soil moisture content above 30%.

Guenzi and McCalla (1962) reported the effect of water-soluble substances extracted from different plant residues on germination and growth of corn, wheat and sorghum while Patrick et al. (1964) showed that water extracts of various plant residues (both with and without soil) decomposed up to 32 days, depress the growth of seedlings. Kimber (1973) indicated that aqueous extracts of several grasses and legumes that had decomposed for periods up to 21 days inhibited the growth of wheat and that the most toxic material from extracts of rye straw decomposed for 4 days had molecular weights from 10,000 to 50,000.

Working on residues of <u>Agropyron</u> <u>repens</u> decaying in soil, Welbank (1963) reported that anaerobic conditions were essential for toxic productions. However, Friedman and Horowitz (1971) reported toxin production under aerobic conditions. From their study with subterranean residues of three perennial weeds, Friedman and Horowitz (1969) concluded that toxin production and degradation occur more rapidly in heavy soil than in light soil. These authors theorized that the faster degradation of organic toxins in heavy soils could be accounted for by the larger production of microorganisms or the higher content of mineral and organic colloids which might have caused adsorption, and hence, inactivation of a greater fraction of the produced toxins.

The information available on the general problem of soil toxicity is still contradictory. Early workers in the field were not able to isolate or identify the postulated toxins. Within the last few years, however, many investigators succeeded in the identification of substances liberated from higher plants. Floyd and Rice (1967) reported inhibition of tomato seedlings by three known bacteria inhibitors-gallatanic acid, gallic acid and chlorogenic acid. Abdul-wahab and Rice (1967) indicated the presence of the inhibitors chlorogenic acid, P-coumaric acid, and P-hydroxybenzaldehyde acid in extracts of Johnson grass rhizomes. Phenolic substances from subterranean parts of purple nutsedge (Cyperus rotundus) were reported by Friedman and Horowitz (1971) to inhibit growth of barley, cotton and mustard.

Manganese Transformations in Flooded Soils

Theory of Redox Potential

Redox Potential (Eh) is the potential which an inert metal electrode (usually platinum) assumes in a solution relative to that of the normal hydrogen electrode. The redox potential gives a direct measure of the oxidizing or reducing intensity of a solution, insofar as the metal electrode responds to and does not interfere with the chemical reaction which gives the solution its oxidizing or reducing character. The potential difference measured is related to the ratio of the activity of the oxidized components of the system to the total activity of the reduced components. It is expressed by the following modification of the Nernst equation (Merkle, 1955):

$$Eh = Eo + \frac{RT}{nF} \ \text{In} \ \frac{[\text{oxidant}]}{[\text{reductant}]}$$

If the usual values are assigned to R (gas constant) and F (value of a Faraday) and the measurements are conducted at 30°C and one electron is involved (n = 1), the equation becomes:

$$eh = Eo + 0.059 \log \frac{[\text{oxidant}]}{[\text{reductant}]}$$

In practice the reference electrode is usually a saturated colomel half cell joined by a liquid function to the solution under test, and the Eh is calculated by adding the reference electrode potential (242 millivolts as compared to the normal hydrogen electrode at 30°C) to the measured voltage.

Since the magnitude of the potential is greatly affected by the acidity of the medium, rising as acidity increases, allowance should be made for the soil pH. To remove pH variability between soils or different horizons in a soil profile, redox potentials are often adjusted to pH_7 by a factor usually -59 MV/pH which corresponds to the transfer of one electron per hydrogen ion in the oxidation-reduction reaction (Aomine, 1964). According to Bohn (1971), the value of -59 MV/pH has little theoretical or experimental justification because of the presence of many redox couples in soil system, but adjustment to a common pH value makes comparisons between different media more convenient. Ponnamperuma (1965) reported that the theoretical conversion factor varied from -30 to -180 MV/pH at 30°C for soil systems, although many workers uncritically used the value -59 MV/pH.

The redox potential is the singular physico-chemical property that differentiates a well-drained soil from a poorly drained one (Rodrigo, 1963). Aerated soils have characteristic redox potentials in the range +400 to +700 millivolts; waterlogged soils exhibit potentials as low as -250 to -300 millivolts. Patrick and Mahapatra (1968) suggested four ranges of redox conditions in soils. At pH_7, oxidized soils are at redox potentials of greater than +400 MV, moderately reduced soils about +100 to +400 MV, reduced soils +100 to -100 MV, and highly reduced soils -100 to -300 MV. Turner and Patrick (1968) reported that the Eh at which oxygen disappeared from several waterlogged soils is in the range of +330 to +350 MV.

The narrow range of redox potential values encountered in well-drained soils and the poor reproducibility caused primarily by a lack of poising of the oxidation-reduction system in the oxidized range (Ponnamperuma, 1955) have resulted in the rejection of the oxidation-reduction potential measurements as a tool for characterizing aeration in well-drained soils. Patrick (1966) gives three factors which combine to make the redox potential the best available measurement of the oxidation or reduction status of waterlogged soils: (1) the range of potential in submerged soils is much wider, approximately 1,000 MV as compared to a range of approximately 300 MV in well-drained soils, (2) in waterlogged soils the higher concentration of reduced components which contributed to the potential result in a better poising and better reproducibility of the potential reading, although poor reproducibility is still one of the main limitations, and (3) oxygen is usually absent from waterlogged soils and the method used for the measurement of oxygen content and oxygen diffusion rate employed in well-drained soils cannot be used in waterlogged soils.

Manganese Reduction under Limiting Oxygen Supply

When a soil is depleted of oxygen by submergence, the reduction of oxidized inorganic soil components is at least somewhat sequential; nitrate and manganic manganese compounds are reduced first, then ferric compounds are reduced to the ferrous form, and last, sulfate is reduced to sulfide (Takai and Kamura, 1966; and Turner and Patrick, 1968).

Manganic oxides undergo reduction in anaerobic soils forming the more soluble manganous compounds (Ponnamperuma, 1965). In terms of redox potentials, Turner and Patrick (1968) reported that Mn began to be reduced at a Eh of +400 MV and was essentially completely reduced at a Eh of +200 MV. According to Mann and Quastel (1946), manganic compounds are reduced by serving as biological electron acceptors or by being reduced chemically by organic compounds during the anaerobic decomposition of organic matter.

A rapid decline in redox potential is characteristic of soils with low content of reducible Fe and Mn and a high organic matter content (Patrick and Mahapatra, 1968). Active Fe and Mn compounds serve as buffers against the development of reducing conditions in soils (Takahashi, 1960). The Mn and Fe systems tend to buffer the soil at an intermediate Eh of +100 to +300 MV. Both systems must be almost completely reduced before intensive reduction can set in. Manganese compounds were found by Nhung and Ponnamperuma (1966) to be the most effective retardants of highly reducing conditions in waterlogged soils.

Other Reduced Substances in Flooded Soils

Under well aerated conditions, the supply of oxygen is adequate to permit complete oxidation of organic materials to carbon dioxide and water, and the mineral constituents of the soil remain almost entirely in an oxidated condition (Black, 1968). But when a soil is flooded with water, the supply of oxygen is rapidly exhausted as a consequence of the reduced rate of gas exchange with the atmosphere (Ponnamperuma, 1965). As a result, there is an accumulation of soluble organic products of microbial metabolism and the conversion of the oxidized soil mineral constituents to their reduced counterparts (Takai et al., 1956 and Sankaram, 1969).

There is evidence indicating the accumulation of various soluble organic acids in waterlogged soils. Among these are formic, acetic, citric, lactic, and valeric acids and methyl mercaptans (Mitsui et al., 1959; Asami and Takai, 1963; and Takijima, 1964).

Oades (1963) states that small chain, low molecular weight organic acids are formed during anaerobic decomposition of organic matter at redox potentials of +100 to +200 MV. According to Tanaka et al. (1961), conditions of high organic matter, high concentration of sulfate, low concentrations of iron, and intensive reduction favor the production of sulfide upon waterlogging a soil.

Effects of Waterlogging

Waterlogging or saturating a soil with water commonly occurs in Louisiana because of high rainfall and poor surface and internal drainage of some soils. The biological and physicochemical changes that accompany waterlogging or submergence (Andreasen, 1952; Christensen et al., 1951; and Copeland, 1957) are important in determining the suitability of the soil for crop production. The availability of several plant nutrients and the production of toxic substances in the soil are influenced by the restriction in soil aeration resulting from submergence.

In the absence of oxygen, facultative anaerobic and true anaerobic organisms utilize oxidized soil components such as nitrate, manganic oxides, ferric oxides, sulfate and assimilation products of organic matter, converting these materials to more reduced forms (Turner and Patrick, 1968; Redman and Patrick, 1965).

Organic matter decomposition is usually slower and less complete under anaerobic conditions. The levels of oxygen supply and the type and amount of organic matter have direct effects on the oxidation-reduction status (Armstrong, 1967; Burrows and Gordon, 1936; Clark and Resnicky, 1956; Mandal, 1961; and Meek et al., 1968).

Fujimoto and Sherman (1948), Christensen et al. (1950), and Gotoh and Yamashita (1966) reported that the reduction of Mn was favored by the presence of readily decomposable organic matter. Reduction of the higher oxides in waterlogged soils takes place when the biological oxidation of organic matter proceeds so rapidly that air cannot supply oxygen in adequate amounts.

Manganese transformations in flooded soils as affected by Eh and pH relationships have also been examined by a number of investigators (Collins and Bual, 1970a and 1970b; Ponnamperuma et al., 1969; and Bohn, 1968, 1970). Most of these studies have been theoretical in nature, probably as a result of the difficulty in controlling both Eh and pH in biologically dynamic systems.

MATERIALS AND METHODS

This study consisted of a series of growth chamber, greenhouse, and field experiments conducted during the period of 1973-1975. Since no published information on similar studies was available, it was necessary to develop practical techniques for several of the tests.

Our approach was to use growth chamber experiments to study techniques and develop general information on optimum moisture levels, organic matter content, and incubation times which would result in maximum Mn reduction. This information formed the basis for greenhouse tests in which an indicator plant (soybean) was used to measure possible effects on growth rates and Mn uptake. The field experiments were also based on the results of the growth chamber studies but used plant residues which were produced by decaying cover crops rather than the added residues used in the greenhouse tests.

Soil Sampling and Chemical Analyses

Soil samples for extractable (water-soluble plus exchangeable) Mn determinations had to be collected while exercising especial care to avoid contact of the soil with air as much as possible and the subsequent oxidation of reduced manganese. Thus, a near-anaerobic method of drawing the soil sample was developed as follows:

Open plastic cylinders, 4 cm in length and capacity for approximately 10 grams of air-dried soil were used for this purpose. The plastic cylinders were pushed vertically into the soil to full length and pulled back (with a soil core inside) with the aid of a knife from underneath the soil. The plastic cylinder, together with the soil sample, was immediately placed in a 250-Erlenmyer flask containing 50 ml of normal ammonium acetate adjusted to pH 4.8 (Cannon, 1971) and capped with a rubber stopper in which a serum cap had been inserted. The serum cap was then punctured with a glass tube attached to a vacuum line and suction was applied to remove the air from inside the flask.

The samples were shaken in a mechanical shaker for 30 minutes and the soil extract filtered through Whatman #2 filter paper. Five ml of HCl were added to the filtered solution to prevent further oxidation of Mn in solution during storage. The Mn content in the solution was determined in the Soil Testing Laboratory using the Perkin-Elmer 503 atomic absorption spectrophotometer.

The extractable Mn content for the growth chamber experiments and for the field experiment (1974 data) was determined colorimetrically by the potassium paraperiodate method as outlined by the Soil Physics Laboratory, Agronomy Department, L.S.U. (unpublished).

Soil pH

Soil pH was determined on the soil samples using the method of Jackson (1958) in a 1:2 soil/water mixture. The pH measurements were made using a Beckman pH meter.

Redox Potential Measurements

Platinum electrodes prepared in the manner described by Fontenot (1972) consisting in fusing a 1-inch piece of 18-gauge platinum wire to one end of a 12-gauge, 4-inch section of copper wire, were used to measure redox potentials. The platinum electrodes were cleaned with fine sand paper prior to use.

Redox potential measurements were made with a portable Beckman Electromate pH meter using a platinum electrode and saturated colomel half cell as reference electrode. The platinum electrodes were pushed vertically into the soil to a depth of approximately 4 cm and remained there for 45 minutes. Redox potential values were converted into millivolts versus the normal hydrogen electrode by adding 242 millivolts to the potential reading.

Plant Sampling and Chemical Analyses

Plant samples consisted of the above ground portion of soybean seedlings. These were dried in a forced-air oven at 70°C for 24 hours and ground in a Wiley mill fine enough to pass through a 20-mesh screen.

A one-gram sample was weighed into a Gooch crucible and ashed in a muffle furnace for 4 hours at 550°C. The ash was dissolved in 10 ml of 50% HCl and the solution was heated on a hot plate until it cleared up and then filtered through Whatman #2 filter paper. The filter paper was washed with hot water several times and the volume brought to 100 ml with distilled water, resulting in 1:100 sample dilution. From this solution, the Mn content was determined without further dilution in the atomic absorption spectrophotometer.

Growth Chamber Experiments

A. Optimum Incubation Period

The objective of this experiment was to determine the optimum incubation period required for maximum release of reduced manganese under high amounts of plant residues and moisture content.

Ryegrass (Lolium perenne L.) was used as the decomposing plant material in this test. A heavy stand of ryegrass was allowed to grow in an Olivier silt loam soil for one month and then killed with paraquat (0.28 Kg/ha.) at a succulent stage. After one week, a block of soil (30 cm x 25 cm x 6 cm) with the dead sod including the roots was placed in a 2-gallon plastic flat of approximately the same size as the soil block. Another plastic flat was filled with adjacent soil in which no plants had been grown. The flats were then saturated with water and placed in the growth chamber at 80^{o}F for 28 days. There were two treatments and four replications in a completely randomized design.

During the incubation period small portions of soil from each flat were withdrawn every four days in the manner described previously and extractable Mn was determined.

B. Optimum Plant Residue Addition and Moisture Level

This experiment was designed to supply and corroborate information related to optimum readily decomposable organic matter content and moisture level for Mn reduction under controlled conditions.

Four soil types were used, namely, Olivier, Sharkey, Commerce, and Convent. The chemical characteristics of the soils are presented in Table 1. The bulk soil samples were obtained from the top portion of the plow layer.

Alfalfa meal, prepared as poultry feed, was used to simulate decomposing plant residues. The chemical analysis of the alfalfa meal is repsented in Table 2.

The hundred grams of air-dried soil were mixed thoroughly with alfalfa meal at 0.1, 0.5, and 1.0 percent by dry weight and placed in 300 grams plastic cups. Water was added to bring the moisture to 15, 30, and 60 percent and incubated in the growth chamber at $80^{o}F$ for eight days. The experiment consisted of nine treatments and four replications arranged in a completely randomized design. After incubation, soil samples were drawn in the method described under the heading "soil sampling," and extractable manganese was determined.

Greenhouse Experiments

This phase of the study consisted of a total of eight greenhouse experiments intended to measure possible toxic levels of soluble Mn in soil using soybean (*Glycine max* L.) as an indicator plant.

One experiment for each of the four soils (Olivier, Sharkey, Commerce and Convent) was established and duplicated sets of data were obtained for 1974 and 1975. Each experiment consisted of eight treatments and four replications in a completely randomized design (Table 3).

Two hundred and fifty grams of soil were mixed thoroughly with Alfalfa meal at 0.0, 1.0 and 2.0% rates and placed in plastic containers (pots) 11 cm in diameter and 5 cm deep. Ten soybean seeds were planted in each pot and water was added to bring the moisture content to 15% during the germination period. After germination, each pot was thinned to

Table 1. Physical and Chemical Characteristics of the Soils Used in the Study

Soil Property	Soil type: Olivier	Sharkey	Commerce	Convent
Texture	Silt loam	Clay	Silt loam	Sandy
pH	6.4	6.8	7.3	7.5
% O.M.	0.88	2.44	1.82	0.31
Extractable Mn (ppm)	10	18	13	8
Extractable P (ppm)	123	256	261	209
Extractable K (ppm)	157	268	196	122
Extractable Ca (ppm)	770	4000+	3160	1090
Extractable Mg (ppm)	78	1000+	711	363

Table 2. Chemical Analysis of the Alfalfa Meal

Property	Percent composition
Fiber	25.0
Protein	17.0
Ash	11.0
Fat	2.0
Calcium	1.5
Phosphorous	0.2

Table 3. Treatments Used in Greenhouse Experiments

Treatment Number	Moisture Percent	Alfalfa meal Percent
1	25*	0.0
2	25	0.5
3	25	1.0
4	25	2.0
5	60**	0.0
6	60	0.5
7	60	1.0
8	60	2.0

*Represents approximately 70 to 80 percent of the water-holding capacity of the soils used.

**Flooded soil conditions.

5 seedlings and water added to bring the moisture content to 25% to one section of pots and to a waterlogged state to the other section of pots during the incubation period. These two soil moisture levels were kept constant by periodical additions of water using the weight difference method.

Soybean seedlings were allowed to grow for eight days, at the end of which time the above-ground portion of each plant was cut and the fresh weight recorded. The plant material was oven-dried, ground, and Mn was extracted as indicated previously.

Soil samples were secured for extractable Mn determination. Redox potential measurements were made by inserting a platinum electrode in each pot after removing the seedlings. The soil pH was determined in the whole volume of soil using a Beckman pH meter.

Another greenhouse experiment was installed aimed to investigate the effect of alfalfa meal concentration on the germination of soybean seedlings. For this experiment, 250 grams of each of Olivier, Sharkey, Commerce, and Convent soils were mixed thoroughly with Alfalfa meal at 0, 0.5, 1.0, 2.0, and 4.0% rates and placed in plastic pots as in the previous experiment.

Nine soybean seeds were planted in each pot and water was added to bring the moisture content to 20%. Each pot was covered with aluminum foil to avoid excess evaporation. Germination counts were made at 3, 5, and 7 days of incubation. The number of germinated seedlings was converted to a percentage of the total seeds originally planted.

Field Experiment

The field experiment was a factorial arrangement of treatments in a randomized block design. Factor A, consisting of three cover crops and a control (no cover crop at all) was placed in the main plots and factor B, composed of three soil types, constituted the sub-plots (Figure 1). The cover crops used were crimson clover (*Trifolium incarnatus* L), ryegrass (*Lolium perenne* L.), and wheat (*Tritium aestirum* L.). The three soil types consisted of Sharkey clay, Commerce silt loam, and Convent sandy loam; all members of the recent alluvial soils of the Mississippi River.

The experiment was established in an Olivier silt loam soil located at the farm of the Horticulture Department, L.S.U., Baton Rouge Campus, in the same site where the multiple cropping experiment (mentioned in the introduction) has been carried out.

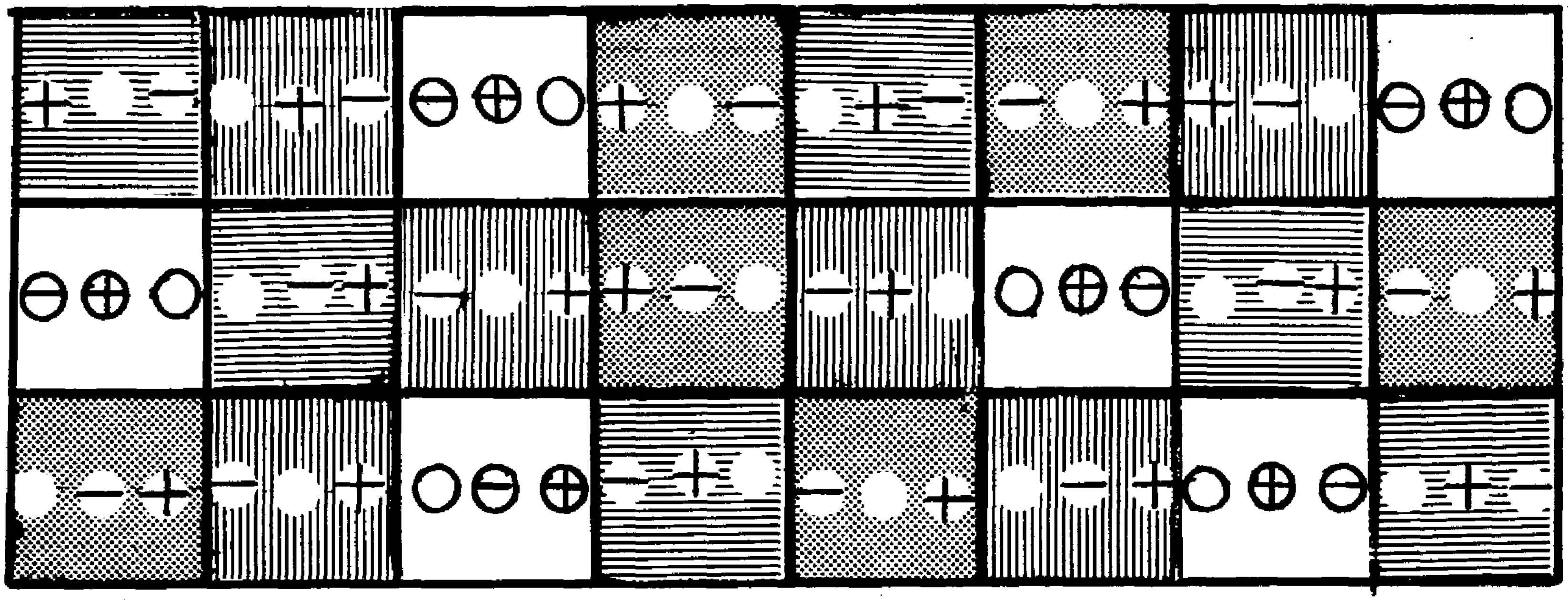


Figure 1. Layout of the field experiment

Seventy-two holes 20 inches apart were opened on the top of three adjacent furrows of Olivier silt loam soil 5 feet apart. The holes were dug out with the aid of a 1-gallon metal can opened at one end and pushed vertically into the soil until reaching a pre-established mark. The final hole was approximately 15 cm in diameter and 8 cm deep. Each hole was then filled with one of Sharkey, Commerce or Convent soil according to the randomization scheme for the sub-plot factor (Figure 1).

The main plots were occupied by the corresponding cover crop or no cover crop at all according to the randomization. The experiment had 12 treatment combinations and 6 replications in a randomized block design.

The 12 treatment combinations were as follows:

1. Crimson clover with Sharkey soil
2. Crimson clover with Commerce soil
3. Crimson clover with Convent soil
4. Ryegrass with Sharkey soil
5. Reygrass with Commerce soil
6. Ryegrass with Convent soil
7. Wheat with Sharkey soil
8. Wheat with Commerce soil
9. Wheat with Convent soil
10. Control with Sharkey soil
11. Control with Commerce soil
12. Control with Convent soil

The soil cores were first set in the field on October 1973 and the cover crops planted in November 1973. The cover crops received a fertilizer application of 8-8-8 formula at 800 Kg/ha. rate two weeks after planting. The control plots were kept weed-free by periodical hand weeding.

On April 30, 1974, the cover crops were killed with paraquat (0.28 Kg/ha.). One week later soybean were planted in the dead sod opening a slit across the furrows. After germination of soybean seedlings, enough water was applied to maintain the soil wet until harvest of seedlings.

Seedlings were harvested on May 22, 1974 and the manganese content determined. Soil samples were collected for determination of extractable Mn and soil pH.

The experiment was continued through 1975. Because some of the soil in each core was used for Mn and pH determinations and also because the "planted soil" tended to mix with the rest of the soil in the plot (Olivier) by both rainfall and mechanical action, it was necessary to open new holes and place new soil cores in the corresponding position occupied by each soil according to the randomization of the 1973 experiment. Subsequent operations were similar to those of the previous year.

Redox potential measurements, in addition to plant and soil Mn and soil pH, were made in the 1975 experiment by means of a portable Beckman Electromate pH meter converted to read redox potential by connecting a platinum electrode.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results will include data from growth chamber, greenhouse and field experiments presented together under four major subtopics. These will be based on the effects of plant residue decomposition (whether applied alfalfa meal or decomposing roots of cover crops) and soil moisture on: (1) soil extractable Mn, (2) soil redox potential, (3) soil pH, and (4) germination, fresh weight and Mn concentration of soybean seedlings.

A. Effects on Soil Extractable Manganese

Data showing the results from the growth chamber experiments are presented in Tables 4, 5, 5a, 5b, and 5c and Figures 2 and 3.

Data in Table 4 show a highly significant increase in soil extractable Mn by adding readily decomposable plant residues (succulent ryegrass plants including the roots) to submerged soil. The maximum amount of Mn released, 680 ppm (Figure 2), occurred at 16 days of incubation. However, this amount of released Mn was not significantly higher than the 648 ppm released at 8 days after incubation. Submergence per se caused significant increases in extractable Mn with time, but it took longer (20 days) to reach the maximum 430 ppm of Mn released in soil.

The mobilization of Mn in soil was very rapid from the beginning of the incubation period, especially in soil containing plant residues. Thus, after four days of incubation, the treatment in which plant material was

Table 4. Soil Extractable Mn as Influenced by Submergence With and Without Decomposing Plant Residues

Incubation time (days)	Extractable Mn (ppm) With plant residues	Extractable Mn (ppm) Without plant residues	Total
0	10	9	19
4	521	192	713
8	642	171	813
12	648	325	973
16	680	319	999
20	644	430	1074
24	584	407	991
28	550	372	922
	4279	2225	

L.S.D. for plant residues at .05 level 28.0, at .01 level 37.4.

L.S.D. for incubation time at .05 level 56.1, at .01 level 74.8.

There was a highly significant interaction.

included contained 521 ppm Mn while the soil without plant residues contained 192 ppm Mn. These represented a 52-fold and a 21-fold increase, respectively, in soil extractable Mn as compared to the initial soil Mn content.

Figure 2 shows two distinct patterns of Mn release depending on whether or not decomposing plant residues were present in the submerged soil. One pattern consists of a striking increase in soil extractable Mn during the first week of incubation, then it levels off for another week and finally starts to decline. This pattern is represented by the treatment containing decomposing plant residues. The other pattern shows a slower but steady increase in extractable Mn released for up to about 20 days followed by a slow decline without indication of a level-off period. This pattern is characterized by the submerged soil without decomposing plant residues.

The observed increase in ammonium acetate extractable Mn during incubation is probably a result of the reducing conditions prevailing during the decomposition and production of intermediate products in submerged soil which are capable of maintaining Mn in a soluble and/or exchangeable forms. The increase in soil extractable Mn by the addition of plant residues was highly significant. This increase was possibly due to the reduction of manganic compounds to a more extractable form as a consequence of the anaerobic metabolism of soil microorganisms which depleted the oxygen from the soil at a faster rate in the presence of readily oxidizable plant residues. Manganic compounds were reduced to the more soluble manganous form either by serving as biological electron acceptors

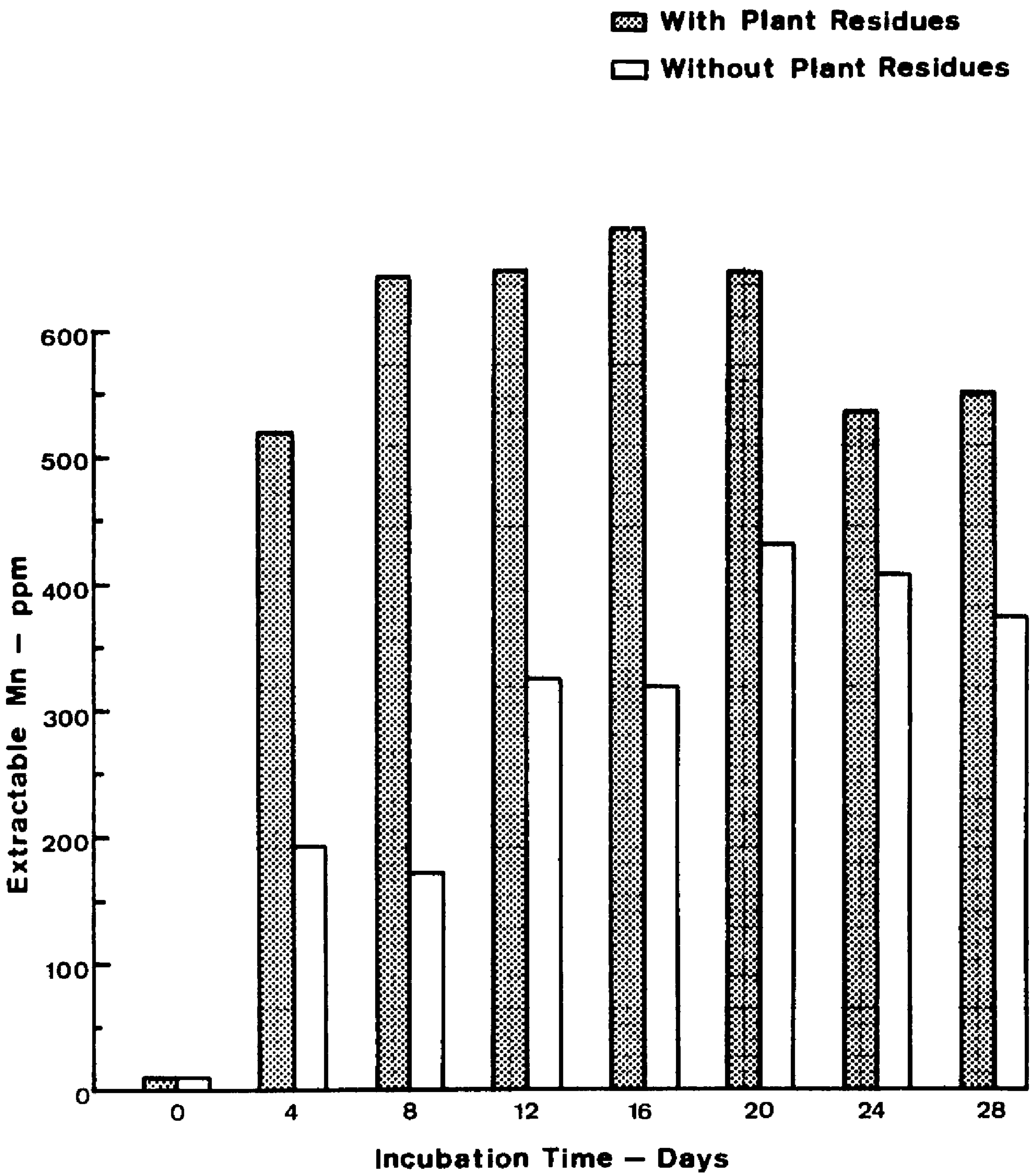


Figure 2. Extractable Mn Content of Submerged Soil With and Without Plant Residues Added

or by being reduced chemically by organic compounds produced during the anaerobic decomposition of organic materials. According to Mann and Quastel (1946), both of these processes occur.

The observed decline in extractable Mn in the soil containing plant material after 16 days of incubation may be the result of insoluble complex formation of soluble Mn with products of plant decomposition after a long period required for the build up of such decomposition products. The slower decline in extractable Mn observed in the soil without plant residues is not properly understood, but it seems that the complex formation with decomposition products of organic matter is slower as the amount of organic residues in this treatment is much less and dependent almost entirely on the amount of native organic matter present in the soil. For Olivier silt loam soil the organic matter content was 0.88 percent.

Data in Table 5 and Figure 3 show the effects of applied alfalfa meal and moisture content on the extractable Mn content of Olivier, Sharkey, Commerce and Convent soils incubated in the growth chamber for one week.

The stastical analyses show highly significant F values for the effects of both alfalfa meal concentration and moisture level, as well as significant interaction between the two factors for Olivier (Table 5a), Commerce (Table 5b), and Sharkey (Table 5c). Only the moisture levels show a significant effect on the extractable Mn content of Convent soil. The presence of significant interaction indicates that the differences between treatment means are due to the combined effects of alfalfa meal concentration and soil moisture content.

Table 5. Influence of Applied Alfalfa Meal and Soil Moisture on Extractable Mn during Incubation

Treatment: Alfalfa meal (%)	Treatment: Moisture (%)	Extractable Mn (ppm): Olivier	Commerce	Sharkey	Convent
0.1	15	3.9	8.8	20.3	2.2
0.5	15	2.8	17.6	27.5	3.3
1.0	15	4.4	37.4	48.4	1.1
0.1	30	102.2	109.9	16.5	44.0
0.5	30	106.1	111.0	26.4	35.2
1.0	30	103.9	124.2	56.1	34.1
0.1	60	316.9	159.4	162.8	90.2
0.5	60	461.5	220.0	255.0	94.6
1.0	60	470.8	269.5	280.4	99.0
L.S.D.	.01	21.6	34.7	24.1	13.5
	.05	16.0	25.7	17.8	10.0

Table 5a. Interaction Effects of Applied Alfalfa Meal and Soil Moisture on the Extractable Mn Content of Olivier Silt Loam Soil

	Moisture level (%): 15	30	60
Alfalfa meal (%)		Extractable Mn (ppm)	
0.1	3.9	102.2	316.9
0.5	2.8	106.1	461.5
1.0	4.4	103.9	470.8

L.S.D. at .05 level 27.7, at .01 level 37.4.

Table 5b. Interaction Effects of Applied Alfalfa Meal and Soil Moisture on the Extractable Mn Content of Commerce Silt Loam Soil

	Moisture level (%)		
	15	30	60
Alfalfa meal (%)		Extractable Mn (ppm)	
0.1	8.8	109.9	159.4
0.5	17.6	111.0	220.0
1.0	31.4	124.2	269.5

L.S.D. at .05 level 44.5, at .01 level 60.0.

Table 5c. Interaction Effects of Applied Alfalfa Meal and Soil Moisture on the Extractable Mn Content of Sharkey Clay Soil

	Moisture level (%)		
	15	30	60
Alfalfa meal (%)		Extractable Mn (ppm)	
0.1	20.3	16.5	162.8
0.5	27.5	26.4	255.0
1.0	48.4	56.1	280.4

L.S.D. at .05 level 30.9, at .01 level 41.7.

The most striking increase in soil extractable Mn from added Alfalfa meal was obtained at the 60 percent moisture level, except for Convent soil which showed no significant increase in extractable Mn from applied Alfalfa meal. The effect of applied Alfalfa meal to soil at 15 and 30 percent moisture seemed inconsistent, and no trend could be followed.

Data from the greenhouse experiments are presented in Table 6 and Figure 4. The term field capacity (Figure 4) is used here with a very loose meaning and indicates a "range" of moisture required for optimum respiration of soil microflora developing in decomposing plant residues. According to Alexander (1961), this range is between 60 and 80 percent of the soil water-holding capacity. The water-holding capacities of the

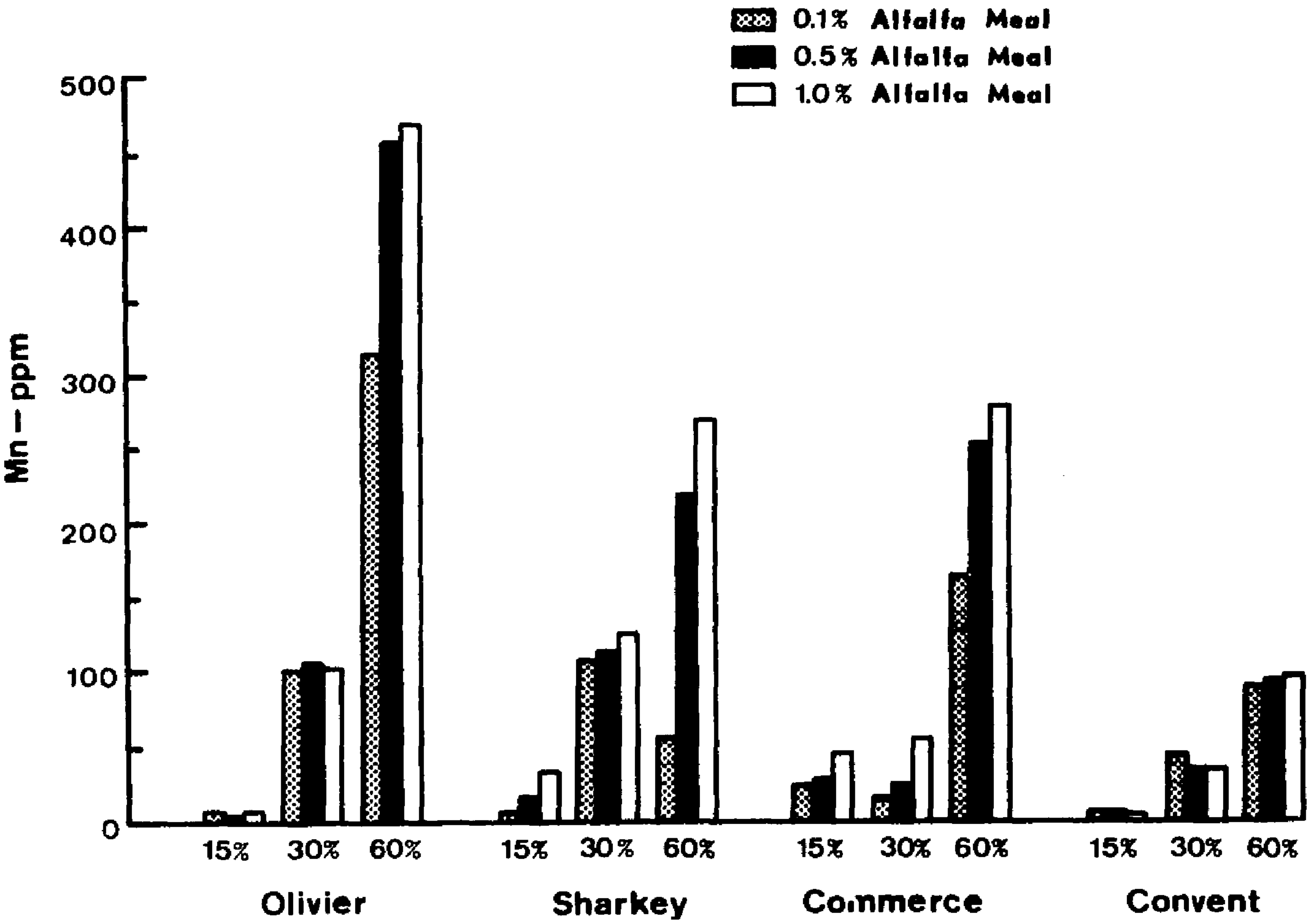


Figure 3. Soil Extractable Mn Content at Three Moisture Levels With 0.1, 0.5, and 1.0% Alfalfa Meal

Table 6. Effect of Alfalfa Meal Additions and Soil Moisture on Soil Extractable Manganese. Sampled in 1974 and 1975

Treatment		Extractable Manganese, ppm							
Alfalfa meal (%)	Moisture (%)	Olivier		Sharkey		Commerce		Convent	
		1974	1975	1974	1975	1974	1975	1974	1975
0	25	13	6	6	9	4	8	6	4
0.5	25	14	6	5	17	5	11	7	4
1.0	25	20	7	7	23	7	17	9	7
2.0	25	34	5	10	32	13	38	11	10
0	60	581	465	125	270	177	133	105	100
0.5	60	691	516	139	299	219	221	104	89
1.0	60	780	647	153	292	234	259	98	97
2.0	60	729	539	145	284	221	240	91	89
L.S.D.	Moisture (%)	34.6**	79.8**	12.6**	12.8**	10.0**	17.4**	13.7**	10.4**
	Alfalfa meal (%)	48.9**	N.S.	N.S.	18.2**	13.0**	24.6**	N.S.	N.S.

*L.S.D. at .05 level of probability.
**L.S.D. at .01 level of probability.

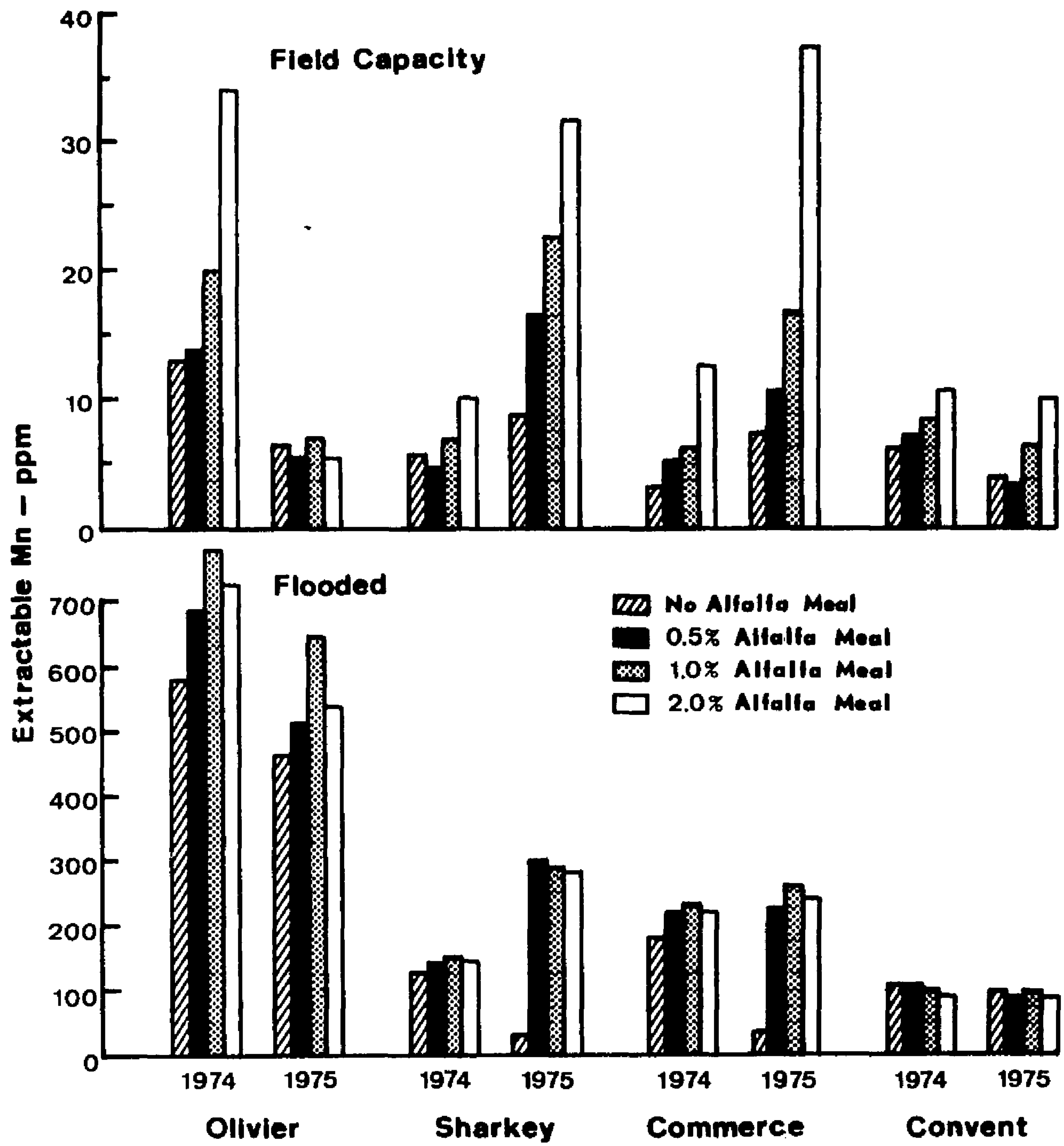


Figure 4. Extractable Mn Content at Two Moisture Levels With 0, 0.5, 1.0, and 2.0% Alfalfa Meal

soils under investigation ranged, approximately, from 30 percent for Convent to 35 percent moisture for Sharkey. The 25 percent moisture level used in this experiment, then, covers a range from 71 to 83 percent of the water holding capacities of the soils under investigation.

As indicated in Table 6, increasing the soil moisture from 25 to 60 percent resulted in a highly significant increase in extractable Mn in all four soils under study. These increases ranged from 568 ppm for Olivier to 99 ppm for Convent soil in the 1974 samples and from 459 ppm and 96 ppm Mn, respectively, for the 1975 samples. The application of Alfalfa meal up to 1 percent to flooded soil (60 percent moisture) resulted in a further increase in extractable Mn released, except for Convent soil.

In general, Olivier soil released the largest amount of extractable Mn followed by Sharkey, Commerce, and Convent, in that order. The capacity of these soils to release Mn must be directly related to the Mn content and solubility of the parent material and secondary minerals which constituted the original components of the soil. Another important factor determining the amount of extractable Mn in soil at any given time is soil pH. In this regard, the observed sequence of soils in descending order of Mn released corresponds to an inverse sequence with respect to pH (Table 1). Thus, Olivier with the lowest pH at 6.4 released the largest amount of extractable Mn, while Convent with the highest pH at 7.5 released the lowest amount of extractable Mn. Sharkey and Commerce were intermediate in soil pH and also in the amount of Mn released.

As summarized in Tables 6a, 5b, and 5c, there was an interaction effect between applied Alfalfa meal and soil moisture. The soil moisture-organic matter-pH interaction effect on Mn transformations is best explained by Leeper (1947) who stated that "a long period of waterlogging at a high temperature can liberate large amounts of soluble Mn. If severe waterlogging is excluded, the bivalent form is favored in strong acid soils, since bacterial oxidation is very slow or absent, whereas organic matter can reduce the higher oxides, again the bivalent form is almost all removed from neutral or alkaline soils since bacterial oxidation is rapid, and reduction by organic matter is now very slow; and in moderately acid soils the bivalent form diminishes with rising pH, since bacterial oxidation rises to a maximum while reduction by organic matter steadily decreases in importance."

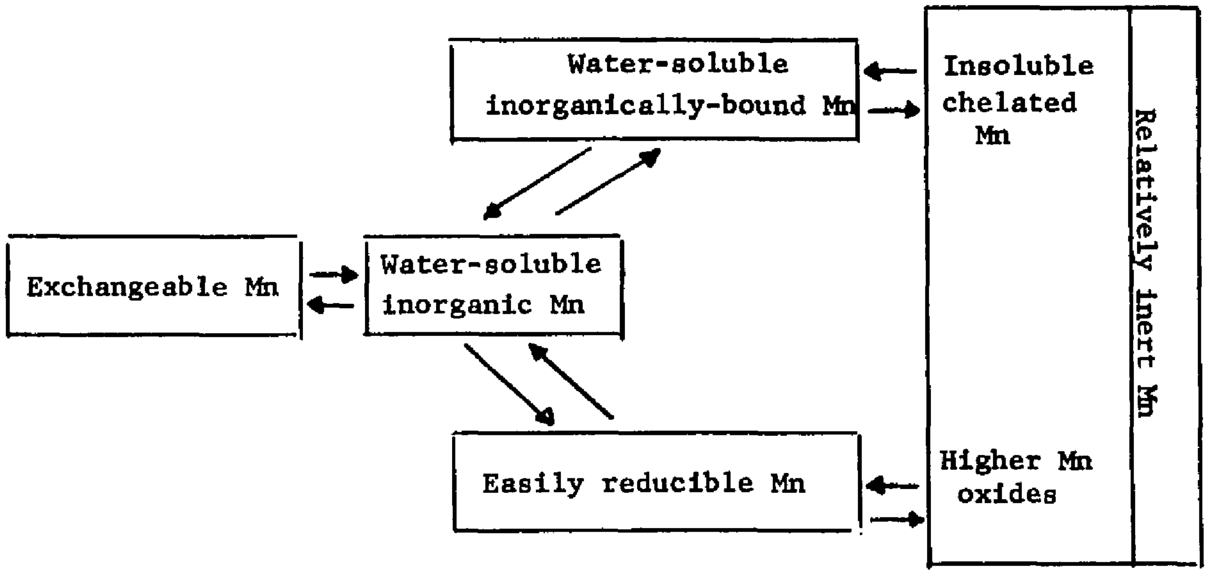
The observed increase in Mn mobilization with flooding is in agreement with previous findings. Redman and Patrick (1965) reported increases in extractable Mn after flooding ranging from 33.6 ppm for a Commerce silt loam soil to 1290 ppm Mn for Olivier silt loam soil. Clark and Resenichy (1956) observed that the Mn level in soil solution of a submerged soil was increased by a hundredfold or more.

As indicated before, the addition of Alfalfa meal to flooded soil further increased the extractable Mn content in all soils except Convent. The explanation advanced in reviewing the results of the growth chamber experiments may apply here also. The lack of response of flooded Convent soil to added Alfalfa meal may be explained on the basis of the low content of native Mn in this soil. Thus, it seems that the reducing conditions created by flooding were intensive enough for Convent soil to release all its fixed Mn.

The lack of response of soils at the lower moisture levels to applied Alfalfa meal and also from flooded Convent soil may be viewed as a lack of soil anaerobiasis related to decomposition products of the Alfalfa meal. It is known that microorganisms of widely different origin are able to produce hydroxy acids from cellulose and other substances of vegetable origin, and the Mn salts of these acids are readily oxidized chemically by the oxygen from the air at pH above 7.0. Therefore, it is possible that the Mn salts produced when Alfalfa meal is added to a well-aerated soil (25 percent moisture and sandy soils) or alkaline soils (as Convent) are oxidized chemically. This explanation is in conformity with Heintze and Mann (1949) who reported that in the saline and neutral soils, organic matter forms complexes with Mn^{++} which are dissociated to a slight extent.

Disagreement among different authors concerning the steps of equilibrium between Mn forms and mechanism of transformations, led to proposals of different Mn cycles. Chanem et al. (1971) proposed a new Mn cycle in order to explain the results of their study in which they showed an increase of Mn reduction when biological oxidation of organic materials was at its maximum rate, and the reduced forms were maintained in spite of the alkaline reaction of the soil. The Mn cycle they proposed is shown on the following page.

Our results are in accordance with this cycle which suggests that in soils two processes that influence Mn transformations are in action. The first is oxidation-reduction; the second is production and decomposition of neutral chelating agents that can combine Mn in soluble or insoluble forms.



The observed differences in extractable Mn content in the same treatment for the same soil from one year to another and the large fluctuations without apparent cause especially at the lower moisture levels seems to be related to the difficulty in maintaining a uniform constant moisture level throughout the incubation period. A special problem is presented by the environmental factors that influence the rate of water evaporation such as radiant energy, temperature and wind. Also, fluctuations tend to be more critical at the lower moisture levels. In addition to the environmental factors, the Alfalfa meal concentration may differentially affect the soil moisture content by affecting the water-holding and cation exchange capacities of the soil. Thus, a soil with applied Alfalfa meal at 2 percent will have a higher water-holding capacity than the same soil without added Alfalfa meal.

Another singular problem is presented by the seasonal variations in Mn content exhibited by soils. According to Hodgson (1963), among the soil elements Mn exhibits the most pronounced seasonal variations in availability, probably due to the microbially induced oxidation and reduction.

Data in Table 7 and Figures 5 and 6 show the effects of decomposing roots of three cover crop species on the extractable Mn content of three soil types under field conditions.

The statistical analyses show that both cover crops and soil type had a significant effect on the concentration of extractable Mn. All cover crops had a significant depressing effect on the extractable Mn content of soil in the 1975 experiment, but only ryegrass depressed significantly the Mn content in soils in the 1974 samples. This variability in the experimental results is difficult to explain and constitutes another example of the difficulties involved when studying soil native Mn. It is also interesting to note the large variations in Mn content in the same soil from one year to another. All three soils showed a significant reduction in extractable Mn content from the 1974 to 1975 samples. It is known that the bivalent form of Mn in soils varies with temperature and rainfall as well as with the length of wet and dry periods. Since it is not possible to control these factors under field conditions, the experimental results must be evaluated in the light of these limitations.

As indicated in the growth chamber and greenhouse experiments, the extractable Mn content varied with soil type, being highest for Sharkey, intermediate for Commerce and lowest for Convent soil.

The significant differences in extractable Mn content observed between the control and the plots containing decomposing plant roots may be

Table 7. Influence of Soil Type and Cover Crop Species on Soil Extractable Mn. Sampled in 1974 and 1975

	Extractable Mn (ppm)							
	Soil type							
	Sharkey		Commerce		Convent		Average	
Cover crop	1974	1975	1974	1975	1974	1975	1974	1975
Clover	250	180	275	159	157	172	227	170
Ryegrass	203	149	162	106	168	126	177	127
Wheat	306	143	268	170	218	89	264	134
Control	288	281	200	231	200	152	229	221
	261	188	226	166	186	134	224	163

1974 - L.S.D. between soil types at .05 level 42.7, at .01 level N.S.
L.S.D. between cover crops at .05 level 49.3.

1975 - L.S.D. between soil types at .05 level 47.6, at .01 level N.S.
L.S.D. between cover crops at .05 level 41.2, at .01 level 54.8.

analyzed from two points of view. First, it may be pictured as a reduction in extractable Mn content in plots under cover crops brought about by insoluble complex formation of soluble Mn under the presence of increased amounts of decomposing plant residues in these plots. It seems reasonable to assume that the higher organic matter content of these plots under cover crops may induce the complex formation of Mn with products of plant residues decomposition. This assumption is supported by Main and Schmidt (1935) who reported that Mn may form chelate complexes with organic matter and by Pavanasosivam (1973) who reported that fixed Mn is significantly and positively correlated with soil humic acid while Misra and Mishra (1969) suggested that fulvic acid may be of

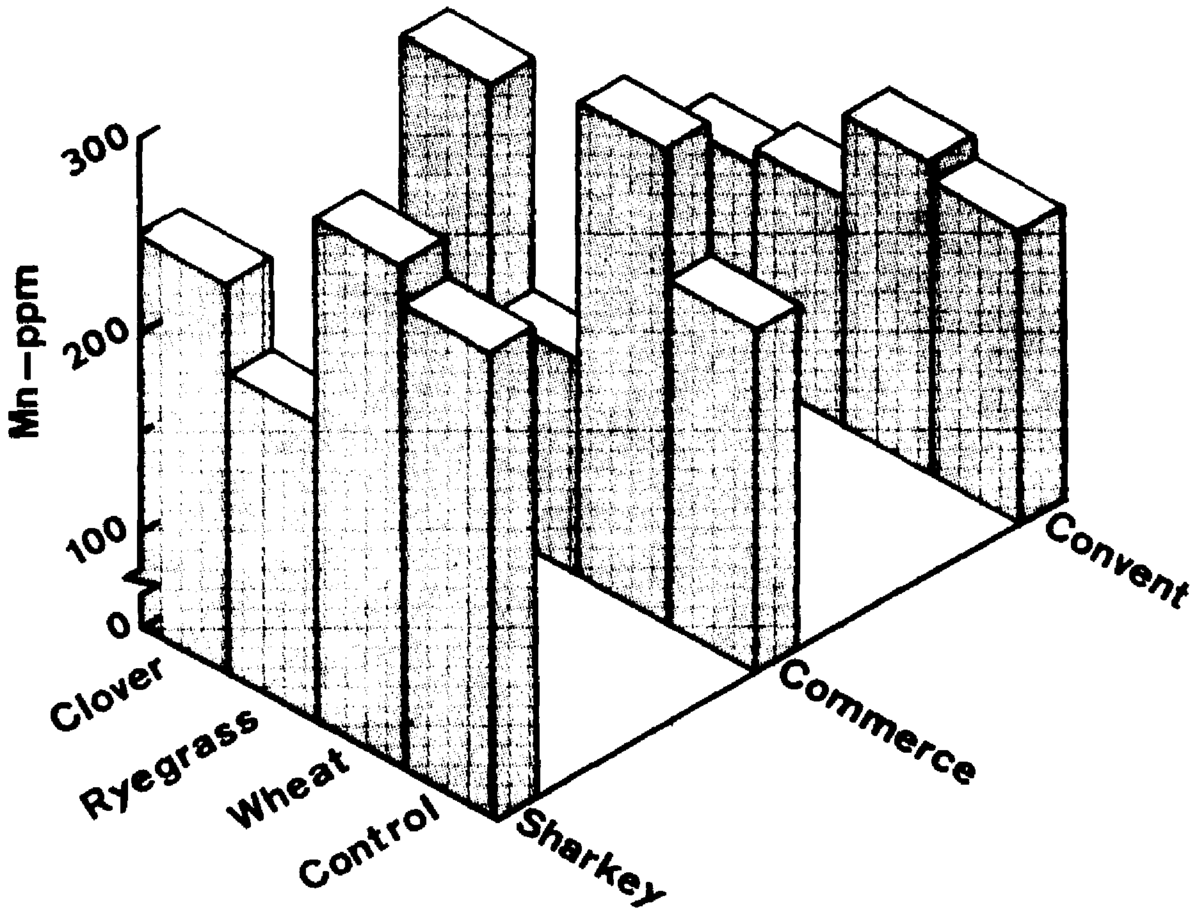


Figure 5. Extractable Mn Content of Three Soil Types Under Three Cover Crops and Control, 1974 Samples

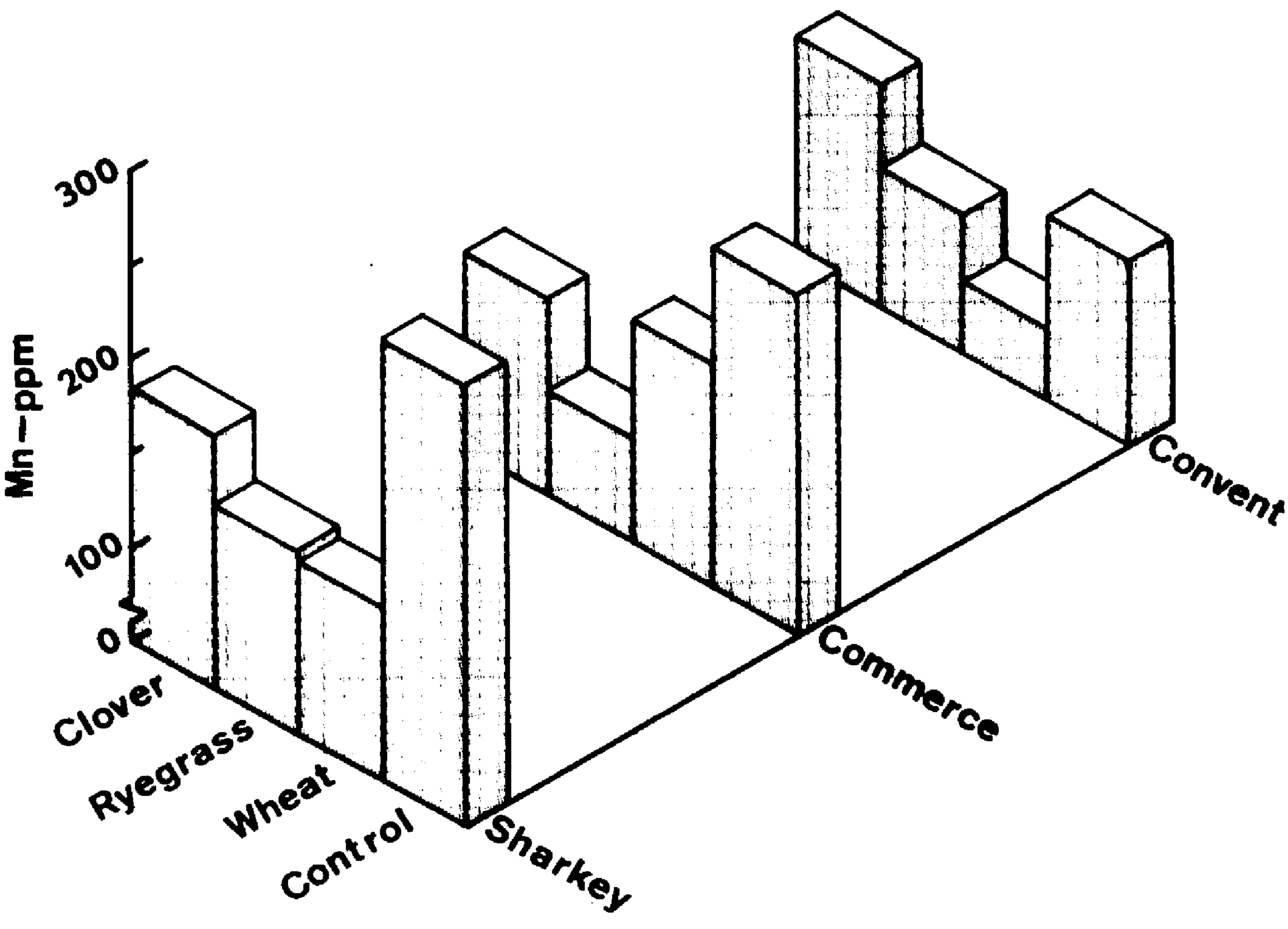


Figure 6. Extractable Mn Content of Three Soil Types Under Three Cover Crops and Control, 1975 Samples

importance in Mn fixation with organic matter. Under this assumption, the decomposing roots of ryegrass seemed to have a higher "complexing power" than the decomposing roots of wheat or clover, especially in the 1974 experiment. This fixation or complexing power may be a function of the amount as well as readiness for decomposition of the supplied plant residues and also a function of quantity of the specific complexing agent present.

A second explanation considers an increase in extractable Mn in the control plots rather than a decrease caused by insoluble complex formation with decomposition products of plant residues. This is primarily an observation of experimental technique rather than a treatment effect, but that may be as valid as the first explanation put forward. As indicated in the section of materials and methods, the field experiment was established in a site of Olivier silt loam soil, which, as it has been demonstrated, can release large amounts of extractable Mn under proper conditions. Therefore, if for any unavoidable reason the soils in the experiment become mixed with the surrounding Olivier soil, it would be reasonable to expect a higher concentration of extractable Mn from the mixed sample. It also appears reasonable to expect a higher soil run-off by rainfall and mechanical action in plots free of cover crops or weeds, such as the control plots and, consequently, more mixing with Olivier soil and higher concentrations of extractable Mn. This applies especially to the 1975 experiment because the seedbeds had become almost flat and the rainfall and irrigation water ran more or less freely over the furrows.

It seems difficult to decide which one of the two advanced explanations best fit the data, especially since the experiment did not provide means of determining the amount of decomposing roots supplied by each cover crop species, neither did it provide means to measure the amount of Olivier soil that might have possibly been mixed with each soil core because that was not the objective of the experiment. Furthermore, it could have been a combined effect of the two factors just discussed.

B. Effects on Soil Redox Potentials (Eh)

Data on the effects of Alfalfa meal additions and soil moisture on the redox potential measurements of Olivier, Sharkey, Commerce, and Convent soils are presented in Table 8 and Figure 7.

There was a rapid decline in soil redox potentials upon flooding. The decline was more pronounced as the concentration of Alfalfa meal increased. The statistical analyses show that the reduction in redox potential due to flooding was highly significant for all soils at the two sampling dates. The application of Alfalfa meal to flooded soils caused a significant further decrease in soil redox potential in all soils, although exceptions from one year to another were evident. The effect of applied Alfalfa meal on the redox potential of soils at 25 percent moisture did not evidence a clear-cut trend and is rather confusing, possibly because of the poor reproducibility of redox potentials on the oxidized range.

Redox potential measurements in flooded soils ranged from 9 to 300 MV indicative of reduced to moderately reduced soil conditions. In the soils at 25 percent moisture, the redox potential measurements ranged from 370 to 622 MV, all of which indicate oxidized soil conditions. However, as stated by Ponamperuma (1955), the narrow range of redox potential

Table 8. Effect of Alfalfa Meal Addition and Soil Moisture on Redox Potential. Sampled in 1974 and 1975

Treatment		Redox potential (MV)							
Alfalfa meal (%)	Moisture (%)	Olivier 1974	Olivier 1975	Sharkey 1974	Sharkey 1975	Commerce 1974	Commerce 1975	Convent 1974	Convent 1975
0	25	454	489	463	529	575	512	622	464
0.5	25	517	522	565	487	542	462	532	429
1.0	25	417	532	535	499	612	444	592	417
2.0	25	370	492	527	487	620	394	592	409
0	60	184	177	140	259	242	300	124	214
0.5	60	44	167	142	99	262	172	114	172
1.0	60	29	189	122	72	207	127	94	104
2.0	60	9	104	67	67	108	64	69	124
L.S.D.	Moisture (%)	63.7**	63.9**	41.1**	43.1**	48.3**	48.0**	44.2**	37.8**
L.S.D.	Alfalfa meal (%)	95.2**	N.S.	42.9*	60.9**	N.S.	67.9**	N.S.	53.5**

*L.S.D. at .05 level of probability.
**L.S.D. at .01 level of probability.

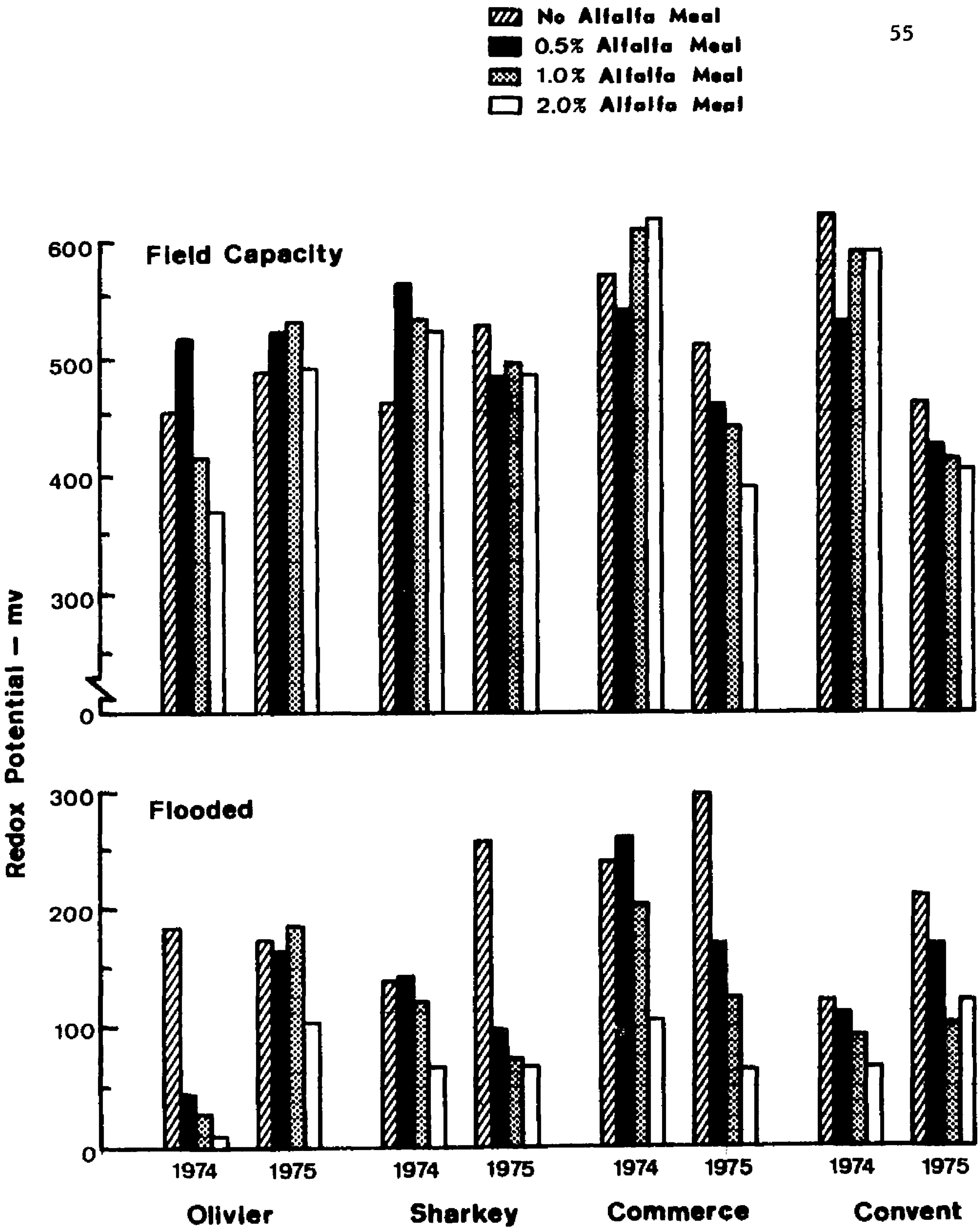


Figure 7. Redox Potential Measurements at Two Moisture Levels With 0, 0.5, 1.0, and 2.0% Alfalfa Meal

values encountered in well-aerated soils and the poor reproducibility caused primarily by a lack of poising of the oxidation-reduction systems in the oxidized range have resulted in the rejection of the redox potential measurements as a tool for characterizing aeration in well-aerated soils.

As indicated earlier, flooding together with Alfalfa meal additions had a marked effect in soil redox potential values. The addition of readily decomposable organic materials to a soil low in oxygen (flooded) stimulates an increase of microbial activity, a rapid and marked drop in the oxygen content of the soil, and an increase in the CO_2 level . The oxygen concentration directly affects the redox potential value and in its absence the potential becomes more negative. Alterations of the Eh are brought about by the consumption of the available oxygen by soil microorganisms and the production of reduced metabolic products.

Most of the chemical changes occurring in flooded soils are associated directly with products of microbial metabolism. Therefore, when oxygen disappears from the soil, the requirements of facultative anaerobic and true anaerobic organisms for electron acceptors result in the reduction of several oxidized compounds in the soil. Nitrate, nitrite, the higher oxides of manganese, hydrated ferric oxides and other ferric compounds and sulfate will be reduced if an energy source is available to the microorganisms.

Manganese and iron have been credited with the capacity to buffer the redox potential of the soil; manganese in the range 100 to -50 and iron in the range -50 to -200 MV (IRRI, 1963). The MnO_2 - Mn^{++} system is of significant importance as a redox system in soil. This is so because of the widespread occurrence of the components of this system in soils, the greater solubility of Mn^{++} than Fe^{+++} or Fe^{++} and the dynamic equilibrium between the manganic and manganous forms of soil manganese.

Our results are in agreement with Patrick (1966) who noted that a rapid decline in redox potential is characteristic of soils having a low content of reducible iron and Mn and high organic matter content, and that Mn and iron systems tend to buffer the soil at an intermediate Eh of 100 to 300 MV, and also with results of Burrows and Gordon (1936), and Andreasen (1952) who reported the development of low redox potentials in waterlogged soils.

The redox potential measurements from the 1975 field experiment are presented in Table 9 and Figure 8. The data show that wetting the soil for five days was very effective in creating reduced soil conditions, as evidenced by the negative values of soil Eh obtained. This is of particular interest considering that during rainy seasons in many tropical and subtropical areas, soils usually remain wet for periods up to several weeks. Under these conditions large amounts of water-soluble and exchangeable Mn may be released, especially in acid soils high in manganese.

Cover crop species had no significant effect on soil redox potential values except for ryegrass which showed a significant increase in Eh. This observed increase in the Eh of plots under ryegrass is difficult to explain, especially when the control plots indicated significantly lower Eh. In fact, should any effect from decomposing plant roots on the soil

Table 9. Influence of Soil Type and Cover Crop Species on Soil Redox Potential

	Redox potential (MV)		
	Soil type		
Cover crop	Sharkey	Commerce	Convent
Clover	11	-14	-72
Ryegrass	54	55	63
Wheat	2	-67	4
Control	-11	-74	4

L.S.D. between cover crops at .05 level 60.1, at .01 level N.S.
L.S.D. between soil types at .05 level N.S.
There was no significant interaction.

redox potential be expected, it would have been a depressing one as observed in the greenhouse experiment with applied Alfalfa meal. A possible explanation for the high Eh in plots under ryegrass could be a lack of uniformity in the distribution of water over the experimental area.

C. Effects on Soil pH

Data in Table 10 and Figure 9 show the effects of applied Alfalfa meal and moisture level on the soil reaction in the greenhouse experiments. The statistical analyses indicate that both Alfalfa meal concentration and soil moisture had a highly significant effect on the soil pH. In general, there was a strong tendency for acid soils to decrease in acidity

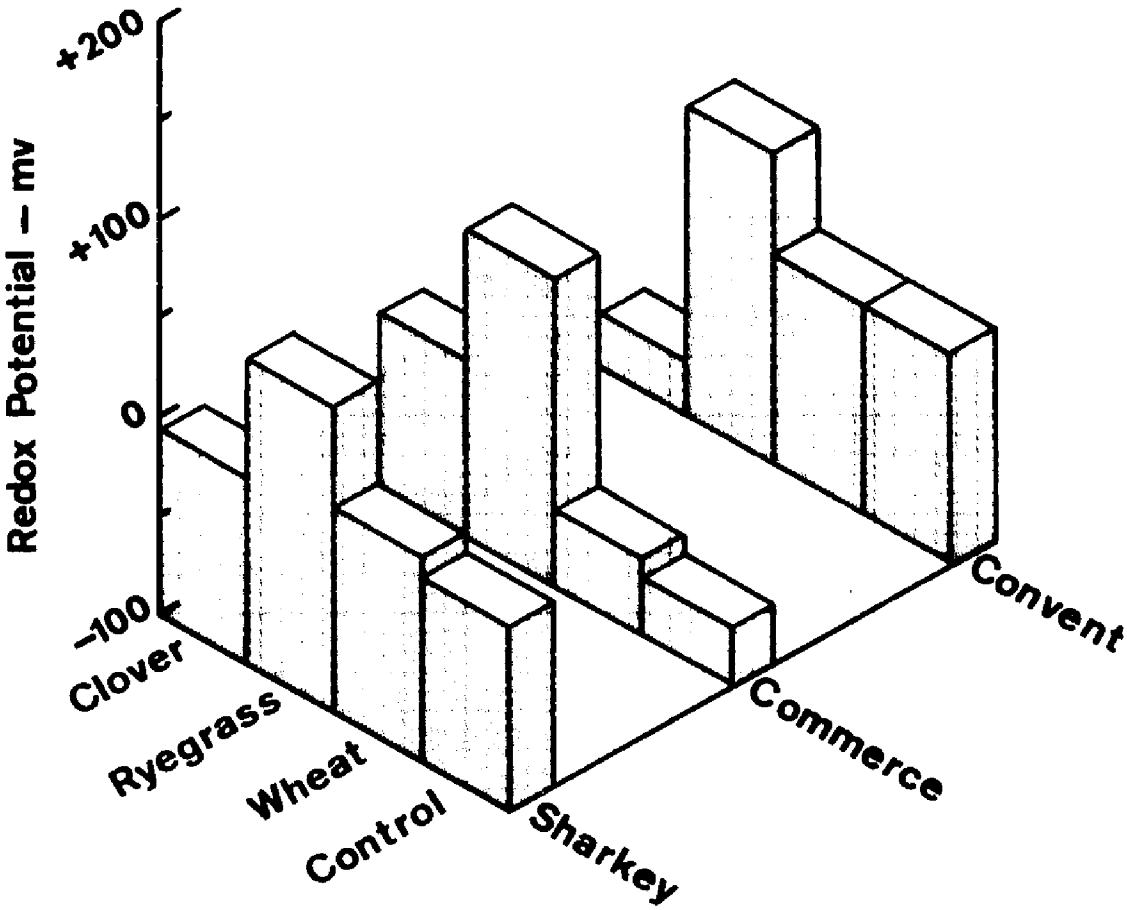


Figure 8. Redox Potential Measurements of Three Soil Types Under Three Cover Crops and Control

Table 10. Effect of Alfalfa Meal Addition and Soil Moisture on Soil pH. Sampled in 1974 and 1975

Treatment			Soil pH							
Alfalfa meal (%)	Moisture (%)		Olivier 1974	Olivier 1975	Sharkey 1974	Sharkey 1975	Commerce 1974	Commerce 1975	Convent 1974	Convent 1975
0	25		6.4	6.0	6.0	6.3	6.4	6.8	7.4	7.4
0.5	25		6.5	6.1	6.2	6.6	6.6	7.0	7.5	7.5
1.0	25		6.7	6.0	6.5	7.0	6.5	6.9	7.4	7.4
2.0	25		7.0	6.3	6.7	7.1	6.8	7.0	7.3	7.4
0	60		7.1	6.5	6.3	6.6	6.6	6.9	7.1	6.8
0.5	60		7.3	6.8	6.6	6.8	6.5	6.9	7.0	6.9
1.0	60		7.4	6.9	6.8	6.9	6.7	6.9	7.0	6.9
2.0	60		7.5	7.1	6.9	7.1	6.9	6.9	7.0	7.0
L.S.D.	Moisture (%)		.11**	.15**	.08**	N.S.	.08**	.05*	.10**	.07**
	Alfalfa meal (%)		.16**	.22**	.11**	.23**	.11**	.07*	.10*	.07*

*L.S.D. at .05 level of probability.
**L.S.D. at .01 level of probability.

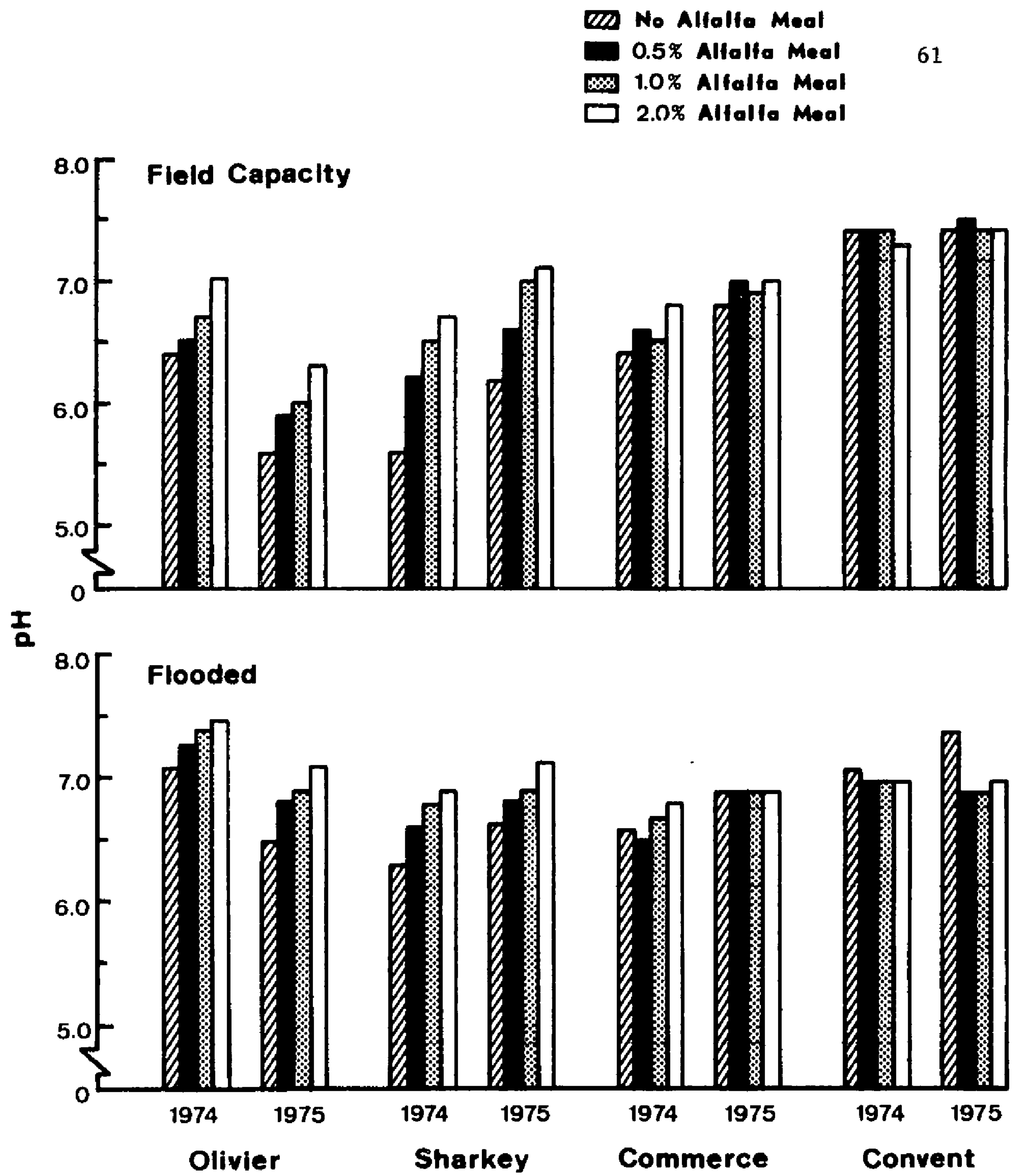


Figure 9. Soil pH at Two Moisture Levels With 0, 0.5, 1.0, and 2.0% Alfalfa Meal

and for alkaline soils to increase in acidity upon flooding. Increasing the concentration of Alfalfa meal in soil further increased the pH of acid soils toward neutrality under both moisture levels. This was true for Olivier, Sharkey, and Commerce soils at both sampling dates. On the other hand, in the alkaline Convent soil, the addition of Alfalfa meal did not show a definite trend.

The increase in pH of acid soils upon flooding may be explained by the formation under reducing conditions of Fe^{++}, Mn^{++}, NH_4^+, H_2S and also $Fe(OH)_2$ and $Mn(OH)_2$ which contribute toward increase in alkalinity as indicated by the following general reactions:

$$FeO_3 + MnO_3 + 6\,HOH \ldots\ldots 2\,Fe(OH)_3 + 2\,Mn(OH)_3$$

$$Fe(OH)_3 + Mn(OH)_3 + 2\,e^- \ldots\ldots Fe(OH)_2 + Mn(OH)_2 + OH^-$$

$$FeS + 2\,H^+ \ldots\ldots Fe^{++} + H_2S$$

The production of ferrous carbonate may account for the observed pH reduction of alkaline soil upon flooding. The additional increase of soil pH caused by applications of Alfalfa meal was probably the result of an increased release of ammonia ferrous iron and manganous manganese. These observations are in agreement with those of Montomura (1962) and Takai et al. (1957) who observed an increase in pH in waterlogged soils and also with Redman and Patrick (1965) who reported a tendency for soils of low pH to decrease in acidity and for soils of high pH to increase in acidity upon submergence.

Data in Table 11 and Figures 10 and 11 show the effects of decomposing roots of three cover crop species on the pH of three soil types under

Table 11. Influence of Soil Type and Cover Crop Species on Soil pH. Sampled in 1974 and 1975

	Soil pH							
	Soil type							
	Sharkey		Commerce		Convent		Average	
Cover crop	1974	1975	1974	1975	1974	1975	1974	1975
Clover	6.11	6.93	6.73	6.94	6.71	7.38	6.51	7.08
Ryegrass	6.28	6.85	6.65	6.90	6.83	7.35	6.58	7.03
Wheat	6.26	6.77	6.58	6.73	6.84	7.25	6.56	6.91
Control	6.48	6.96	6.63	6.81	6.84	7.41	6.65	7.06
	6.28	6.87	6.64	6.84	6.80	7.34		

1974 - L.S.D. between soil types at .05 level .08, at .01 level .10.
L.S.D. between cover crops at .05 level .08, at .01 level N.S.

1975 - L.S.D. between soil types at .05 level .12, at .01 level .17.
L.S.D. between cover crops at .05 level N.S.

Table 11a. Interaction Effects of Decomposing Roots and Soil Type on pH. Sampled in 1974

	Soil type		
Cover crop	Sharkey	Commerce	Convent
Clover	6.11	6.73	6.71
Ryegrass	6.28	6.65	6.83
Wheat	6.26	6.58	6.84
Control	6.48	6.63	6.84

L.S.D. at .05 level .15, at .01 level .20.

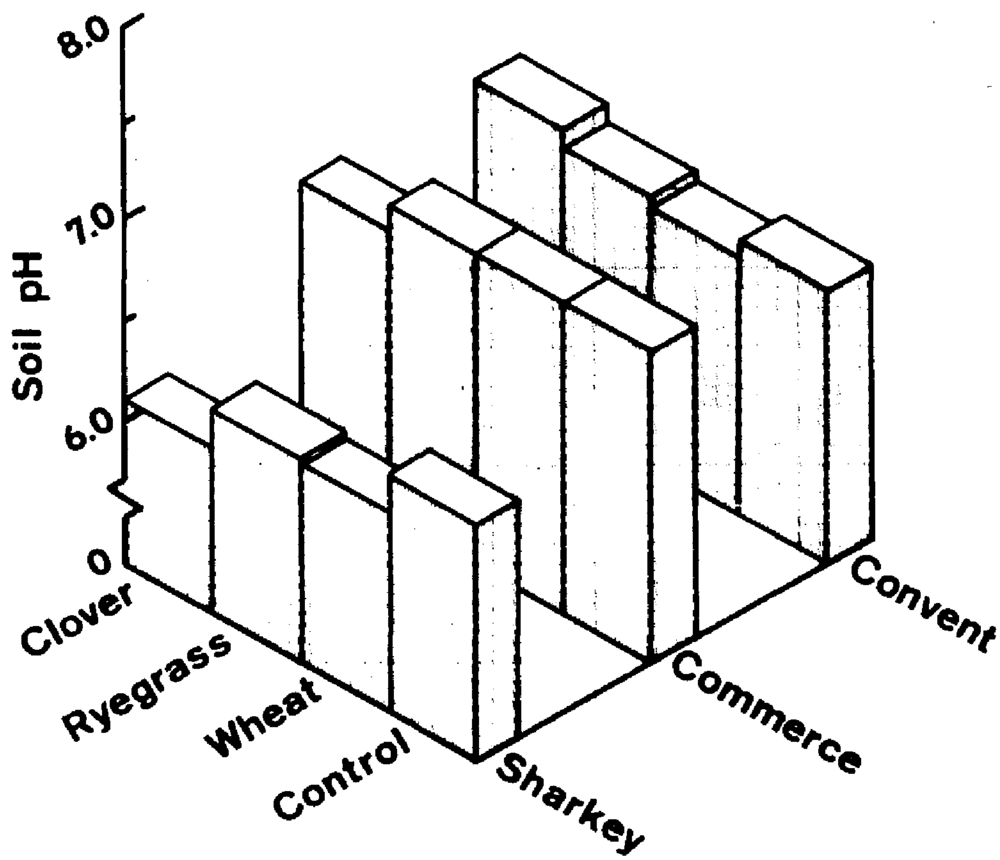


Figure 10. pH of Three Soil Types Under Three Cover Crops and Control, 1974 Samples

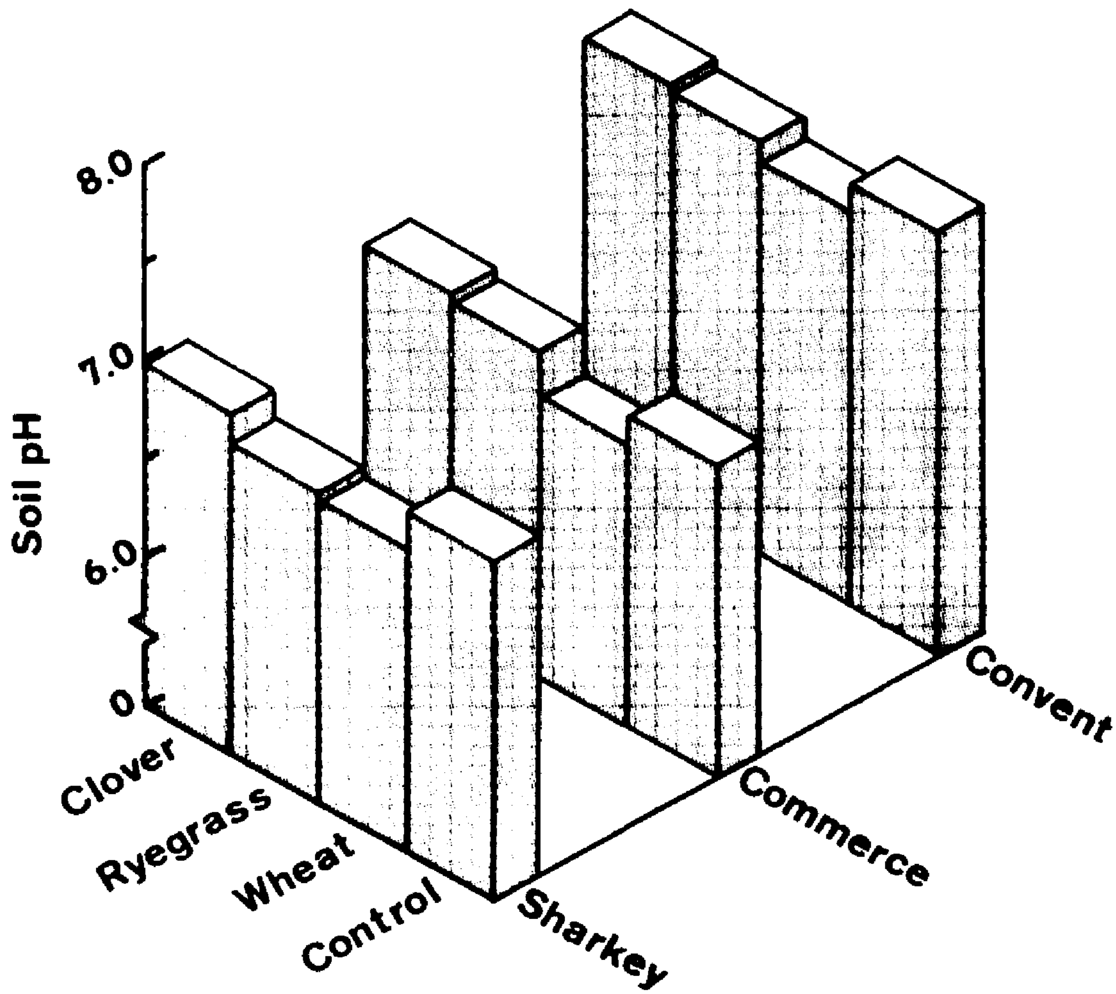


Figure 11. pH of Three Soil Types Under Three Cover Crops and Control, 1975 Samples

field conditions. The difference between pH mean values indicated interaction effects between cover crops and soil types for the 1974 sample (Table 11a). Thus, the pH values of Sharkey for the control plots were significantly higher than those under cover crops, and the pH value for plots under clover was significantly lower than that of plots under wheat or ryegrass. For Commerce soil only the difference in pH value between clover and wheat was significant while the pH values of Convent soil showed no significant differences. These observed interaction effects are not properly understood and, again, seem to be the result of an uneven distribution of water over the experimental site.

In the 1975 samples, only differences in pH among soil types were significant which was to be expected, considering the fairly large differences in the original pH of the soil under study. The cover crops had no effect on the soil pH in the 1975 samples.

Even though the statistical analyses indicated significance among pH differences, these differences do not appear to be large enough to have a significant effect on the release of soil extractable Mn, except when the pH value of one soil type is compared to another, especially between Sharkey and Convent soils. Therefore, we may conclude that the decomposing roots of cover crops did not appear to have a significant effect on the release of soil extractable Mn via soil pH.

D. Effects on Soybean Seedlings

1. Germination and Fresh Weight

The effects of Alfalfa meal concentrations on the germination of soybean seedlings grown in four different soil types is summarized in Table 12.

The percent germination was markedly reduced by added Alfalfa meal, especially at 2 and 4 percent concentrations. The reduction in germination was highly significant in all soils under study but was more pronounced in Olivier silt loam in which the germination was reduced from 88 to 44 percent with the addition of 2 percent Alfalfa meal and to 30 percent with 4 percent Alfalfa meal after seven days of incubation. Four percent of applied Alfalfa meal was required to cause a significant reduction in the final stand of germinated seedlings in Sharkey, Commerce and Convent soils. However, the germination was significantly slowed down when Alfalfa meal was applied at rates of 2 and 4 percent. Thus, while the percent germination in the control treatment ranged from 74 to 100 percent through the incubation period, that of the 4 percent Alfalfa meal treatment ranged from 5 to 63 percent for the same period.

The results showing the effects of Alfalfa meal additions and soil moisture content on the fresh weight of soybean seedlings are summarized in Table 13 and Figure 12. The fresh weight of seedlings was generally reduced by flooding and by increasing the concentration of Alfalfa meal in soil, although exceptions were observed. Thus, increasing Alfalfa meal concentration showed no significant reduction in the fresh weight of seedlings grown in Convent or Commerce soils for the 1974 samples, while

Table 12. Effect of Alfalfa Meal Concentration on Germination of Soybean Seedlings During Incubation Time

Treatment		Percent germination — Time of incubation (days) — Olivier 3	Olivier 5	Olivier 7	Sharkey 3	Sharkey 5	Sharkey 7	Commerce 3	Commerce 5	Commerce 7	Convent 3	Convent 5	Convent 7
Control		68	88	88	100	100	100	74	77	83	83	83	83
0.5% Alfalfa meal		61	72	83	68	72	88	57	74	85	85	91	91
1.0% Alfalfa meal		44	72	83	83	85	85	50	68	74	88	91	88
2.0% Alfalfa meal		16	41	44	63	80	88	30	50	72	41	74	74
4.0% Alfalfa meal		5	11	30	44	63	63	38	50	52	18	50	41
L.S.D. for	.01		8.35			13.57			11.02			8.50	
Incubation time	.05		6.31			9.25			8.32			6.42	
L.S.D. for	.01		10.79			16.08			14.23			10.98	
Alfalfa meal (%)	.05		8.15			12.15			10.75			8.29	

Table 13. Effect of Alfalfa Meal Additions and Soil Moisture on the Fresh Weight of Soybean Seedlings. Sampled in 1974 and 1975

Treatment		Fresh weight, g/seedling							
Alfalfa	Moisture	Olivier		Sharkey		Commerce		Convent	
meal (%)	(%)	1974	1975	1974	1975	1974	1975	1974	1975
0	25	1.17	1.39	1.28	1.23	0.97	1.03	0.87	0.86
0.5	25	1.08	1.26	1.10	0.96	1.07	1.06	0.94	0.91
1.0	25	1.04	1.18	1.03	0.92	1.08	1.10	0.77	0.83
2.0	25	0.86	1.19	0.97	0.93	1.16	1.09	0.76	0.82
0	60	1.16	1.10	1.08	1.27	1.29	1.24	1.14	1.28
0.5	60	1.15	1.12	1.12	1.07	0.96	1.22	1.25	1.38
1.0	60	1.02	0.95	0.78	1.02	1.04	0.95	1.31	1.41
2.0	60	0.68	0.82	0.74	0.84	0.73	0.77	1.18	1.02
L.S.D.	Moisture (%)	N.S.	.17**	.14*	N.S.	N.S.	N.S.	.15**	.17**
	Alfalfa meal (%)	.12**	.18*	.26**	.19**	N.S.	.17**	N.S.	N.S.

*L.S.D. at .05 level of probability.
**L.S.D. at .01 level of probability.

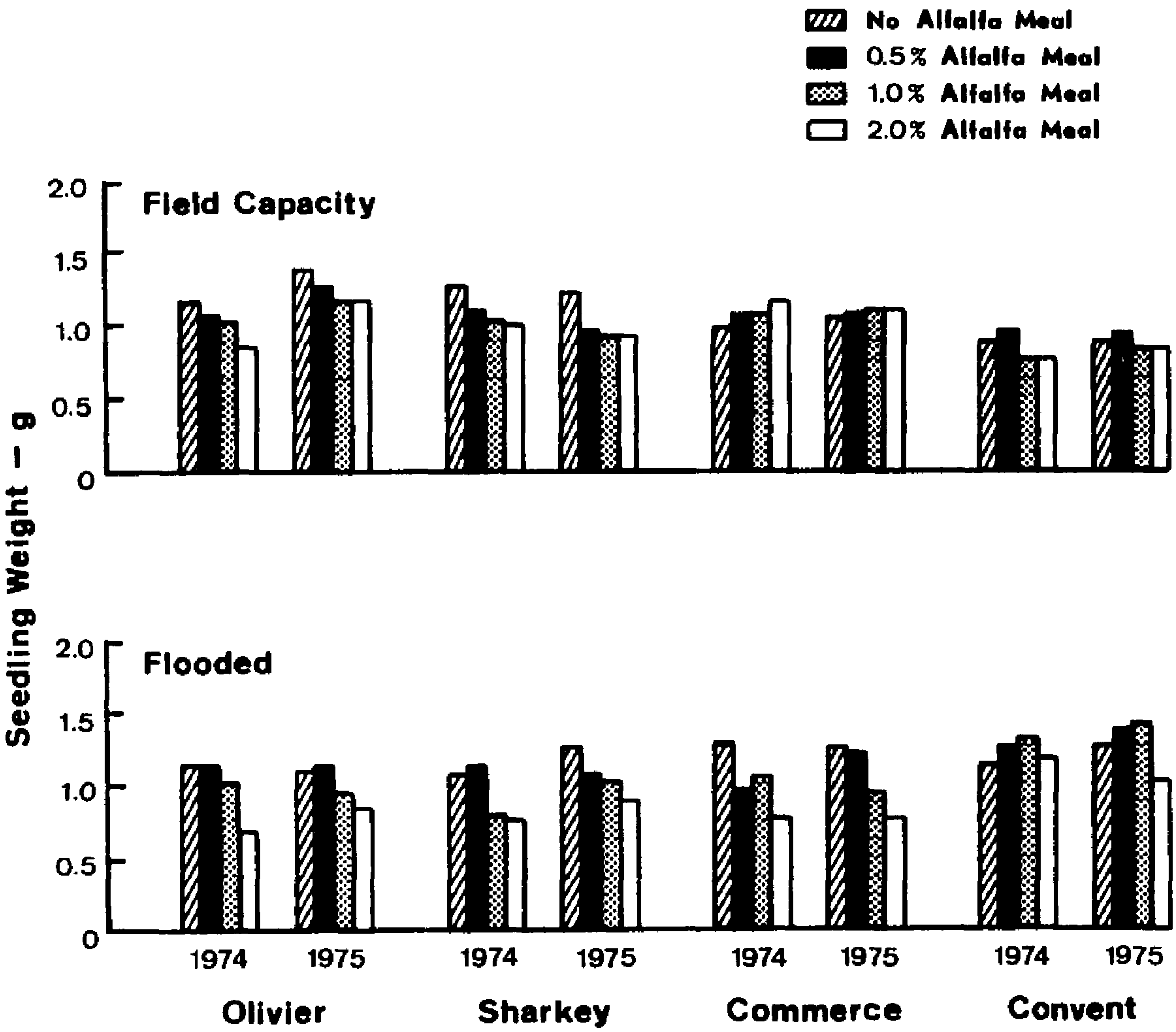


Figure 12. Fresh Weight of Soybean Seedlings Grown at Two Moisture Levels With 0, 0.1, 1.0, and 2.0% Alfalfa Meal

flooding caused an increase in fresh weight of seedlings grown in Convent soil. The depressing effect of applied Alfalfa meal on the fresh weight of soybean seedlings was more pronounced under flooded conditions.

Applied Alfalfa meal at 2 and 4 percent rates caused a delayed and depressed germination of soybean seedlings in all four soils under investigation. The precise mechanism whereby decomposing plant residues affect seed germination is not clearly understood and at the present time only educated guesses may be advanced. One possible manner by which decomposing organic residues may affect seed germination is by curtailing the oxygen supply to the seed and the emerging seedling, resulting in a reduction or complete stop of respiration because of oxygen depletion. The addition of readily decomposable plant residues to the soil stimulates an increase in microbial activity and a rapid and marked drop in the oxygen content of the soil. If the amount of added plant residues is large enough, above 4 percent, a sudden and dramatic depletion of soil oxygen may be expected immediately following its application. This oxygen depletion is more likely to occur in localized areas around the germinating seed where the oxygen demand is very high as compared to the surrounding soil.

Another manner in which decomposing plant residues may affect seed germination is by the formation of toxic substances. In this connection, Toussoun et al. (1967) reported that some phytotoxic effects noted from substances produced during decomposition of organic matter were an inhibition or delay of seed germination, seed killing, necrosis of roots, and inhibition of root growth and root hair development of tobacco, lettuce, and bean seedlings. The production of soil toxins will be considered in more detail when discussing the effects of applied Alfalfa meal on fresh weight of seedlings.

Since the germination experiment was not originally designed to investigate the possible factors that may have affected seed germination, no definite conclusions can be drawn from the results obtained. However, some general observations can be made. In the first place, the observed depressing and delaying effect on seed germinations from applied Alfalfa meal tend to bias the results on the fresh weight of seedlings as well as the results on the uptake by soybean seedlings based on the premise that the bioassay is not uniform to begin with. As a consequence, the use of indicator plants to determine the effect of applied plant residues on the growth and mineral uptake by seedlings will provide biased results unless the proper germination and seedlings' stand is obtained after controlling the "germination depressing factor."

In spite of the above results and bearing in mind its limitations, the data on the effects of plant residues and soil moisture on the fresh weight and Mn concentration of soybean seedlings will be discussed in the following paragraphs.

The contention that phytotoxic substances released during the decomposition of plant residues, especially under high soil moisture content, might be the triggering mechanism whereby the germination and subsequent growth of soybean seedlings are affected is well documented. For example, McCalla and Haskins (1964), Patrick and Koch (1958), and Patrick and Toussoun (1965) have noted that the decomposition of plant organic matter in soil is often accompanied by formation of substances with phytotoxic properties. Patrick et al. (1963) reported that the most severe phytotoxicity occurred in fields where decomposition of plant organic matter had taken place in cold, wet soil during early stages of decomposition. Guenzi and McCalla (1962) reported the effects of water-soluble substances extracted from different plant residues on germination and growth of corn, wheat and sorghum.

Among the reported toxic substances are: benzoic, phenylacetic, 3-phenyl propionic and phenyl butyric acids (Toussoun et al., 1967); chlorogenic acid, P-coumaric acid, and P-hydroxybenzaldehyde (Abdul-Wahab, 1967); and the bacterial growth inhibitors gallic, gallotanic, and chlorogenic acids (Floyd and Rice, 1967).

Applied Alfalfa meal had little or no depressing effect on the fresh weight of seedlings grown in Convent sandy soil, except possibly for the 2 percent rate. This may be explained on the basis of soil texture and native organic matter content. Convent is a light sandy soil with low clay and very little organic matter content (0.31 percent) and, consequently, low cation exchange capacity and low microbial population, also, low content of mineral and organic colloids. The above mentioned soil characteristics would seem more suitable for a slower decomposition of plant residues and a slower production of toxic substances than the heavier Sharkey soil for example. According to Friedman and Horowitz (1969), the toxin production and degradation occur more rapidly in heavy soil than in light soil.

2. Manganese Concentration in Soybean Seedlings

Table 14 and Figure 13 show the data on the effects of Alfalfa meal and soil moisture on the Mn concentration of soybean seedlings. Particularly striking is the increase in Mn uptake by seedlings grown in flooded Olivier soil which was several times higher than the Mn uptake by seedlings grown in any of the other flooded soils (Figure 13). Flooding increased the Mn concentration of seedlings in all soils under study. The Mn concentrations was, generally, highest in seedlings grown in Olivier soil, intermediate for those grown in Sharkey and Commerce, and lowest in seedlings grown in Convent soil. This sequence of soils according to the Mn concentration of seedlings corresponds to a similar sequence based on the amount of extractable Mn released suggesting a possible relationship between soil extractable Mn and the Mn concentration of soybean seedlings.

The effect of Alfalfa meal concentration per se in the Mn uptake by soybean seedlings appears to be extremely variable and no clear cut trend can be followed. It seems, however, that at the high moisture content (60 percent), high concentrations of Alfalfa meal in soil were associated with high Mn concentration of seedlings, except for Olivier soil. Large variations in Mn concentrations of seedlings among sampling dates were evident. This lack of uniformity of the experimental results regarding the Mn concentration of seedlings may be a consequence of the observed detrimental effects from applied Alfalfa meal on the germination and growth of seedlings.

Data in Table 15 and Figures 14 and 15 show the effects of decomposing roots of cover crops on the Mn uptake by soybean seedlings grown

Table 14. Effect of Alfalfa Meal Additions and Soil Moisture on the Concentration of Mn in Soybean Seedlings. Sampled in 1974 and 1975

Treatment		Mn concentration, ppm							
Alfalfa meal (%)	Moisture (%)	Olivier 1974	Olivier 1975	Sharkey 1974	Sharkey 1975	Commerce 1974	Commerce 1975	Convent 1974	Convent 1975
0	25	190	109	59	66	57	47	54	44
0.5	25	140	100	55	69	49	49	47	50
1.0	25	70	93	48	67	50	51	43	54
2.0	25	80	131	49	79	55	47	41	47
0	60	380	395	102	76	108	73	76	72
0.5	60	300	288	116	79	144	84	66	76
1.0	60	390	231	131	103	136	89	68	85
2.0	60	490	266	122	86	202	137	83	100

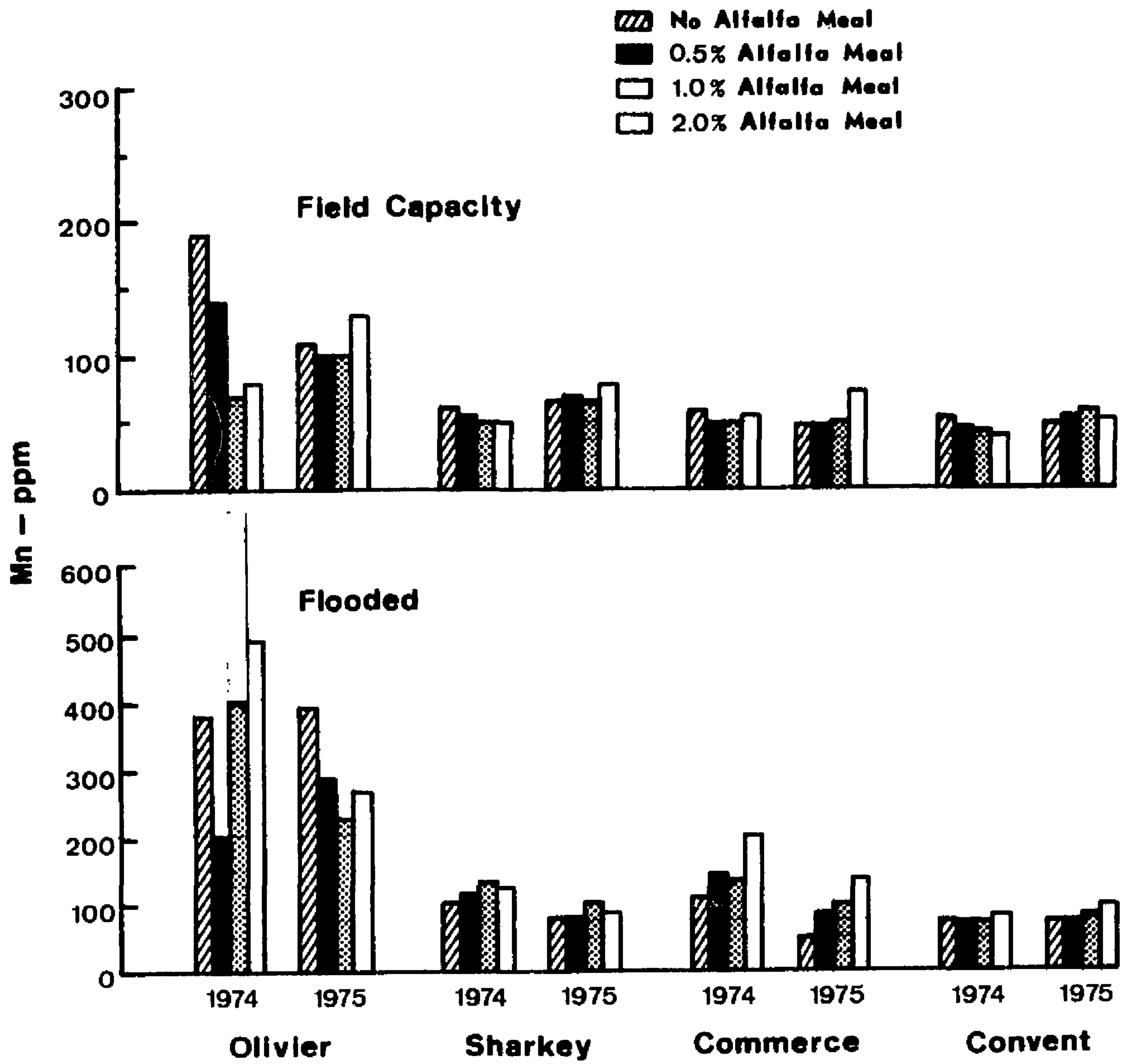


Figure 13. Manganese Concentration of Soybean Seedlings Grown at Two Moisture Levels with 0, 0.5, 1.0, and 2.0% Alfalfa Meal

Table 15. Influence of Soil Type and Cover Crop Species on the Concentration of Mn in Soybean Seedlings. Sampled in 1974 and 1975

	Mn concentration, ppm							
	Soil type							
	Sharkey		Commerce		Convent		Average	
Cover crop	1974	1975	1974	1975	1974	1975	1974	1975
Clover	96	97	104	96	94	111	98	101
Ryegrass	79	95	86	93	104	102	89	97
Wheat	84	86	84	83	90	93	86	90
Control	137	122	129	113	136	138	134	124
	99	101	101	97	106	111		

1974 - L.S.D. between soil types at .05 level N.S.
L.S.D. between cover crops at .05 level 13.6, at .01 level 18.1.

1975 - L.S.D. between soil types at .05 level N.S.
L.S.D. between cover crops at .05 level 16.2

in three soil types under field conditions. Soybean seedlings grown in the absence of decomposing roots (control) showed a significantly higher Mn concentration than those grown in plots with decomposing plant residues. There was no significant difference in Mn concentration of seedlings among cover crop species or soil types. The increased Mn concentration in seedlings grown in the control plots seems to be associated with the higher concentration of extractable Mn in the control plots.

The data on Mn concentration in seedlings failed to furnish definite evidence to attribute a significant role to decomposing plant residues (whether applied Alfalfa meal or plant roots) on the concentration of Mn in soybean seedlings. Furthermore, the data failed to supply evidence

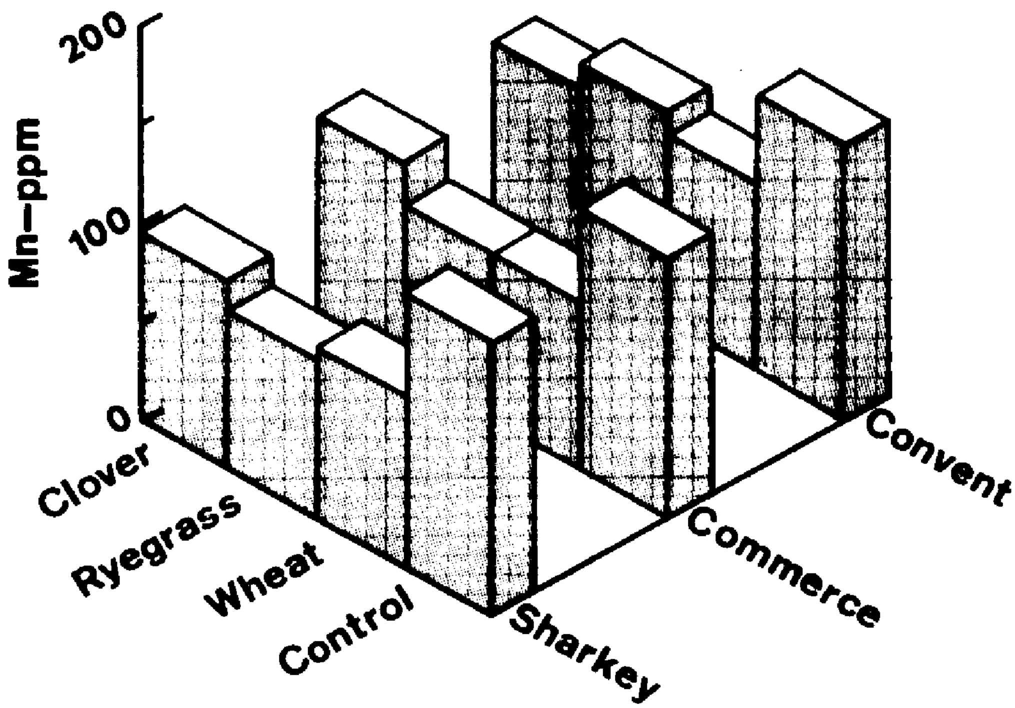


Figure 14. Manganese Concentration of Soybean Seedlings Grown in Three Soil Types Under Three Cover Crops and Control, 1974 Samples

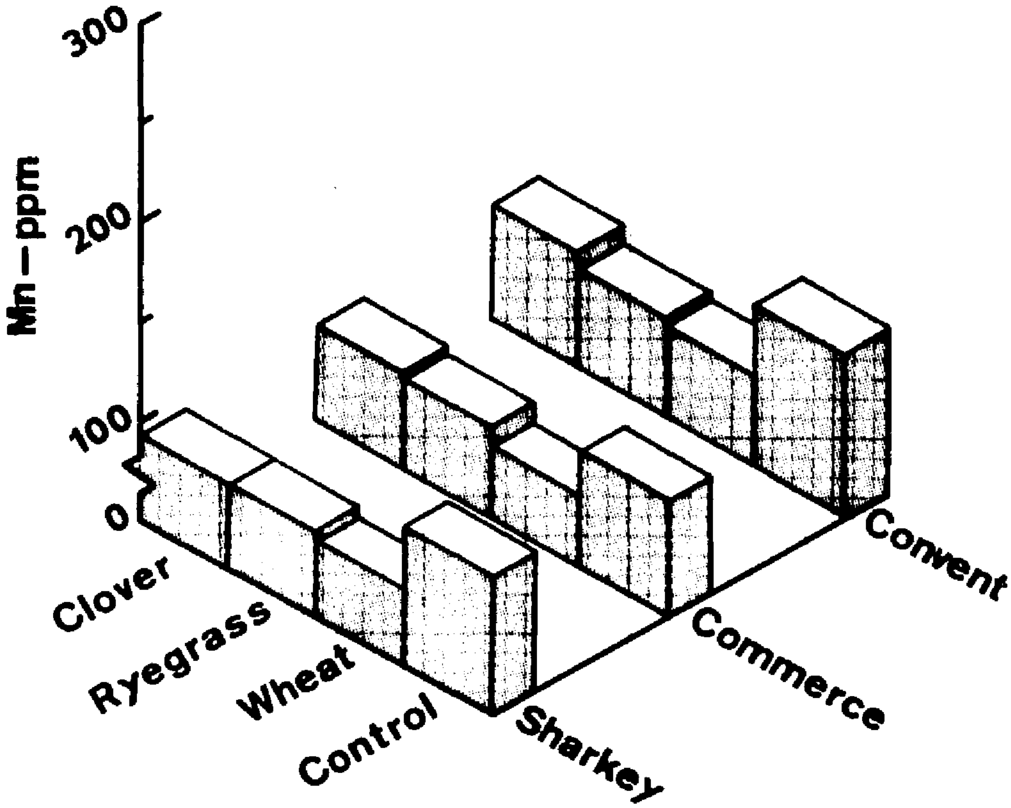


Figure 15. Manganese Concentration of Soybean Seedlings Grown in Three Soil Types Under Three Cover Crops and Control, 1975 Samples

to implicate Mn as a possible cause of the observed depression of seedling germination and growth.

Although the writer found no reference in the literature pertaining to the critical levels of Mn in soybean seedlings' tissue, Robertson et al. (1973) observed that the highest yields of soybeans were obtained when the Mn content in the leaves was 72 ppm. They also reported that when soybean leaves had Mn content of 119 ppm, yields were lower, possibly because of toxic amounts of Mn. However, the Mn values for soybean seedlings recorded in this investigation appears low in comparison with those reported for other species of plants.

Standifer (1973) reported Mn concentration in southern pea seedlings showing Mn toxicity ranging from 5,000 to 12,000 ppm. Sherman and Fujimoto (1946) reported that an abnormality of lettuce grown on acid soil could be controlled by liming. The Mn content of the lettuce plants was 3,800 ppm compared to that of 760 ppm in the healthy plants. Cannon (1971) reported Mn toxicity to sweet potato plants in sulfur-treated plots at concentrations ranging from 5,000 to 12,000 ppm, but no Mn toxicity symptoms were present when the Mn concentration in the leaves was 1,000 ppm.

The fact that the Mn concentration in soybean seedlings was generally low, except for those grown in flooded Olivier soil, and because there was no visible evidence of Mn toxicity symptoms in the developing seedlings, it seems reasonable to assume that some other factor or factors were responsible for the observed reduction in growth of soybean seedlings. If Mn toxicity was involved, then its effect was not strong enough to show its toxic symptoms visually.

Soil moisture showed a pronounced effect on the Mn concentration in seedlings (Table 14). Flooding the soil caused, on the average, a near two-fold increase in Mn concentration in seedlings as compared to the soil at 25 percent moisture. This increase in Mn concentration seems to be associated with the striking increase in soil extractable Mn caused by flooding. Especially high was the Mn concent of seedlings grown in flooded Olivier soil which, again, seemed to be associated with the high content of extractable Mn exhibited by this soil as compared with the rest of the flooded soils. The magnitude of the difference in Mn uptake by seedlings grown in Olivier soil as compared to the other soils appears to be in the same order of the difference in extractable Mn content between Olivier and the other soils. Thus, the extractable Mn content for flooded Olivier soil as an average of all Alfalfa meal rates was 695 ppm and 542 ppm for the 1974 and 1975 samples, respectively (Table 6), and the corresponding Mn concentration in seedlings was 390 and 295 ppm (Table 14). The corresponding figures for Convent soil are 100 and 94 ppm of extractable Mn and 73 and 83 ppm of Mn in seedlings.

The relative uptake of ions by plants is determined in part by the relative availabilities of the ions in the soil. Relative availability of Mn, however, does not necessarily correspond closely with relative concentration of the extractable ion in soil, probably because of the complicated dynamic equilibirum of Mn in the soil. However, these data account for a relative association between soil extractable Mn and the Mn concentration in soybean seedlings.

In this respect, Leeper (1947) dismissed total Mn in the soil as irrelevant to the problem of the deficiency disease "gray speck" of oats and "marsh spot" of peas. Adams and Wear (1957) showed that the development of "crinkle leaf" (Mn toxicity) in cotton was related to the level of water-soluble Mn in soil. Forsee (1954) working with organic soils in Florida found water-soluble Mn less reliable than exchangeable Mn in determining the amount of Mn taken up by the plant. Stenuit et al. (1956) could find no relationship between water-soluble Mn of various soils and the occurrence of "gray speck" of oats.

In the field experiment where the decomposing roots of the various cover crop species (rather than applied Alfalfa meal) constituted the readily oxidizable plant organic material, it was seen that the presence of such decomposing plant residues caused a significant reduction in the Mn concentration of soybean seedlings (Table 15). Expressed in other terms, soybean seedlings grown in the control plot had a significantly higher concentration of Mn than seedlings grown in plots containing decomposing plant root residues. However, the Mn uptake by seedlings was not significantly affected by cover crop species.

The above reported effects of decomposing plant roots under field conditions on the Mn concentration in soybean seedlings are in disagreement with those reported earlier for applied Alfalfa meal in the greenhouse experiment which showed no significant effects from added Alfalfa meal on the Mn uptake by seedlings. A possible explanation for the lack of agreement on the effects of the two sources of organic residues on the Mn uptake by seedlings may be that Alfalfa meal and plant roots are different in their chemical composition, thus affecting the rate of decomposition and also the decomposition products may be different. However, the mechanisms whereby the two sources of plant residues may affect the Mn uptake by seedlings is not understood.

Large amounts of organic matter in the soil have been reported by Nishita (1956) to reduce Mn uptake by plants. Agboola and Corey (1973) reported the Mn concentration in maize tissue to be highly negatively correlated with soil pH and percent organic matter. If we assume that the plots under cover crops were supplied with larger amounts of organic residues than the rates of Alfalfa meal used in the greenhouse experiment, then the above findings provide an explanation for the observed uptake by seedlings. However, this assumption is completely speculative considering that the amount of plant residues supplied by each cover crop species was not determined.

The regression coefficient for Mn concentration in soybean seedlings as dependent variable and soil extractable Mn, pH and redox potential as independent variables showed no significant association in the field experiment. The F value of the partial regression analysis between Mn uptake by seedlings and soil extractable Mn was significant. Considering that the extractable Mn is the sum of water-soluble plus exchangeable Mn in soil, we can reasonably conclude that the observed positive relationship between extractable Mn and the concentration of Mn in soybean seedlings is in agreement with Adams and Wear (1957) who reported that the development of "crinkle leaf" in cotton was related to the level of water-soluble Mn in soil and with the findings of Rich (1956) who found a highly significant correlation between exchangeable soil Mn and the Mn concentration in the upper leaves of peanut, and also with Cannon (1971) who found a highly significant association between extractable soil Mn and the Mn concentration in sweet potato leaves.

SUMMARY AND CONCLUSIONS

The effect of high concentration of decomposing plant materials with incubation on the extractable Manganese content of submerged acidic Olivier silt loam soil was investigated in the growth chamber. A marked increase in soil extractable Mn upon submergence was observed. This increase was more pronounced and more rapid in the treatment containing decomposing plant residues.

The incubation technique in the growth chamber and the greenhouse was used to investigate the effects of rates of organic amendments (Alfalfa meal) and soil moisture level on the concentration of soil extractable Mn, pH, and redox potential as well as the effects on germination of soybean seedlings. The following general conclusion can be drawn from the results attained:

1. Increasing the soil moisture from 25 to 60 percent resulted in two striking increases in soil extractable Mn content, especially in Olivier silt loam soil. Less marked increases were observed for Sharkey, Commerce and Convent soils.

This order of soil types based on the descending amounts of Mn released corresponds to an increasing order of the initial pH of the soils involved.

2. Adding Alfalfa meal in concentrations up to one percent to flooded soils further increased the relee e of extractable Mn in Olivier, Sharkey and Commerce soil but had no significant effect on flooded Convent soil or on any of these soils at a lower moisture level.

The lack of response to added Alfalfa meal to soil at low moisture levels is because the oxygen concentration in the soil was not low enough to allow any significant reduction of Mn. The lack of response of flooded Convent soil seems to be associated with the low concentration of native Mn in this soil.

3. Parallel to the increase in soil extractable Mn, flooding induced a rapid decline in the soil redox potential to levels characteristic of reduced soil conditions. This decline of the redox potential was more pronounced in the presence of increasing concentrations of Alfalfa meal.

The decline of redox potential by flooding is the result of the exclusion of soil air by water and the resulting oxygen depletion. The addition of organic material increases microbial activity resulting in higher respiration and faster depletion of soil oxygen.

4. At low soil moisture (25 percent) the redox potential measurements ranged from approximately 400 to 600 MV, characteristic of well-aerated oxidized soil.

5. There was a strong tendency for soils of low pH to decrease in acidity and for soil of high pH to decrease in acidity upon flooding. Addition of Alfalfa meal to the soil favored the development of higher pH.

This strongly suggests that the pH of soils tend to be buffered around neutrality by substances produced as a result of flooding. Among these are the production of hydroxyl ions as a result of the reduction of ferric and manganic compounds and the production of ammonia as well as ferrous carbonate and ferrous hydroxide.

6. Flooding increased the Mn concentration of soybean seedlings. Seedlings grown in Olivier soil were highest in Mn, those grown in Sharkey and Commerce were intermediate, and those grown in Convent soil showed the lowest concentration of Mn in the tissue.

This descending order of soil types based on the amount of Mn uptake by seedlings is similar to the descending order based on the amount of soil extractable Mn. This strongly suggests that the Mn uptake was directly associated with the amount of soil extractable Mn.

7. There was no clear evidence suggesting any significant effect from the addition ofAlfalfa meal on the uptake of Mn by soybean seedlings.

8. Concentrations of Alfalfa meal in the soil above 2 percent showed a significant depressing effect on the germination of soybean seedlings in all soils under study.

9. Increasing the concentration of applied Alfalfa meal in the soil caused a corresponding reduction in the vegetative yield of soybean seedlings, except for those grown in Convent soil. The reduction in vegetative yield was more pronounced under flooded conditions.

The depressing effect of applied Alfalfa meal on the germination and vegetative yield of soybean seedlings seemed to be associated with the production of toxic substances from the products of Alfalfa meal decomposition.

Even though the highest vegetative yields were generally associated with the lowest Mn contents in plant tissue, the observed depressed yield can hardly be ascribed to Mn toxicity, particularly when the Mn contents in some good-yielding plants were several times as high.

A special technique was developed for the field experiment. The significant feature of this technique is that it provides a feasible means of studying several soil types together in a small replicated field experiment. The following conclusions can be drawn from the field experiment.

1. There was a significant reduction in the extractable Mn content of soils planted to a cover crop as compared to the control plots. It was theorized that the increased concentration of decomposing plant residues (mainly roots) supplied by the cover crops may have formed insoluble complexes with soluble Mn in the soil.

2. There was no significant difference among cover crops in the extractable Mn content in the soils

3. Wetting the soils for a 5-day period created redox potential values characteristic of reduced soils high in extractable manganese. This finding is of special significance considering that wet soils for periods of one or two weeks are common in Louisiana during the rainy season. At the observed redox potential values, most of the soil manganese is expected to be in the water-soluble and exchangeable forms.

4. The pH of the soils under cover crops was significantly reduced. The increased production of CO_2 from the higher concentration of decomposing plant residues in these plots and the subsequent production of carbonic and other acids may account for this pH reduction.

5. There was a reduction in Mn uptake by soybean seedlings induced by decomposing crop roots. This reduction in Mn concentration of

seedlings seemed to be associated with a reduction in the extractable Mn and pH of the soils under cover crops.

6. The F value for the partial regression for the association between manganese uptake by seedlings and soil extractable manganese approached significance. It showed significance at the 5.6 percent level of probability as compared to the 5 percent commonly used. However, there was no significant linear relationship between Mn uptake by soybean seedlings and soil pH or redox potential.

The present investigation has shown that substances with phytotoxic properties may be formed during the decomposition of plant residues in the soil. This confirmation of the production of phytotoxic compounds during the decomposition of plant residues is of special interest because of the suspected importance in crop succession in a multiple cropping system. Since these have been laboratory and greenhouse experiments mainly, the interpretation as to the possible significance of the results presented must be viewed in the light of these limitations.

Whether the toxic factor(s) from decomposing plant residues in the soil observed in this study can also be produced under field conditions or affects plants in the manner indicated in such complex systems of the soil environment cannot be definitely stated at this time.

It is possible, therefore, that toxic decomposition products may occur in soils and under conditions which, when considered as a whole, would not appear to favor their production. In such instances these substances are likely to be produced in localized areas where concentration of plant residues, water content, soil pH and other factors are

are favorable for the type of breakdown leading to toxin formations.

Our data failed to establish any significant relationship between the extractable Mn content in soil and the observed reduction in germination and yield of soybean seedlings. This, however, does not rule out completely the possible involvement of Mn as a toxic agent. What we can conclude is that our experiment was not critical enough to detect its possible involvement.

It was shown in this study that high moisture content in the soil leads invariably to high levels of extractable Mn which under certain conditions and crop species may be toxic to developing plants.

This investigation was directed toward finding out whether decaying vegetative matter could cause an increase in soil extractable Mn and thus be a contributing factor in the development of Mn toxicity. This could be of particular importance when minimum tillage is used to permit efficient cropping under high rainfall conditions. The results from redox potential measurements show that this could be a contributing problem. Extractable Mn may also be involved under very wet soil conditions, and yet tissue analysis seems to indicate that it is not a limiting factor.

It appears that we should conclude that decaying vegetation could cause higher levels of extractable Mn, particularly under wet conditions. We have not shown, however, that this could increase Mn uptake by soybean seedlings, but because of technique problems, we are not able to show that it does not affect levels of plant Mn.

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AUTOBIOGRAPHY

Antonio Velez was born on February 20, 1937 in San Lorenzo, Puerto Rico, where he was graduated from high school in 1956.

He received his B.S. degree in General Agronomy from the University of Puerto Rico, Mayaguez Campus, in December, 1960 and his M.S. degree in Horticulture from Louisiana State University in January, 1970.

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EXAMINATION AND THESIS REPORT

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Major Field: Horticulture

Title of Thesis: Some Effects of Decomposing Plant Residues and Soil Moisture on the Extractable Manganese Content of Four Soil Types

Approved:

Leon C. Standifer
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Date of Examination:

August 25, 1975